

การออกซีไดซ์โทลูอินด้วยไฮโดรเจนเปอร์ออกไซด์ที่อุณหภูมิสูง
บนตัวเร่งปฏิกิริยา TS-1 ที่ได้รับการดัดแปลง



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TOLUENE OXIDATION BY HYDROGEN PEROXIDE AT ELEVATED
TEMPERATURE OVER MODIFIED TS-1



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งานวิจัยนี้ทำการศึกษาปฏิกิริยาออกซิเดชันระหว่างระหว่างโทลูอินร่วมกับไฮโดรเจนเปอร์ออกไซด์โดยมีตัวเร่งปฏิกิริยาไทเทเนียมซิลิกาไลต์-1 ในระดับอุณหภูมิที่สูงกว่าจุดเดือดของน้ำที่ความดันบรรยากาศ ตัวเร่งปฏิกิริยาได้รับการปรับปรุงโดยการเติมโลหะอะลูมิเนียมในปริมาณต่าง ๆ ทำการวิเคราะห์ตัวเร่งปฏิกิริยาที่สังเคราะห์ได้ด้วยเครื่อง X-ray Fluorescence Spectroscopy (XRF), X-ray Diffractometer (XRD), Fourier Transform Infrared Spectrometer (FT-IR), nitrogen adsorption (Brunauer-Emmett-Teller - BET) และ Temperature Programmed Desorption of ammonia (NH₃-TPD) ปัจจัยที่ทำการศึกษาคือ ปริมาณโลหะอะลูมิเนียมที่เติมเข้าไป อุณหภูมิในการทำปฏิกิริยา และอัตราส่วนโดยโมลของไฮโดรเจนเปอร์ออกไซด์ต่อโทลูอิน ผลการทดลองแสดงให้เห็นว่าอะลูมิเนียมที่เติมเข้าไปในตัวเร่งปฏิกิริยาไทเทเนียมซิลิกาไลต์-1 ไม่ไปทำลายโครงสร้างของตัวเร่งปฏิกิริยา และการเติมอะลูมิเนียมจะช่วยเพิ่มการเกิดเบนซอลดีไฮด์ให้มากขึ้น ตัวเร่งปฏิกิริยาที่ได้รับการปรับปรุงทุกตัวให้ผลิตภัณฑ์หลักเป็นเบนซอลดีไฮด์ โดยมีออโร-ครีซอล และพารา-ครีซอลเป็นผลิตภัณฑ์ข้างเคียงในปริมาณเล็กน้อย ผลการทดลองยังแสดงให้เห็นว่า การเพิ่มอุณหภูมิในการทำปฏิกิริยา จะทำให้อัตราการเกิดปฏิกิริยาเพิ่มขึ้น แต่ในบางกรณีจะทำให้ค่าร้อยละการเปลี่ยนแปลงของไฮโดรเจนเปอร์ออกไซด์ไปเป็นผลิตภัณฑ์ลดลง นอกจากนี้การเพิ่มอัตราส่วนโดยโมลของสารตั้งต้นระหว่างไฮโดรเจนเปอร์ออกไซด์ต่อโทลูอินจะทำให้เกิดเบนซอลดีไฮด์เพิ่มมากขึ้น

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This research studies the oxidation of toluene by hydrogen peroxide using titanium silicalite-1 catalysts modified with different amount of Al at the reaction temperatures higher than the boiling point of water at atmospheric pressure. All catalysts are characterized by X-ray Fluorescence Spectroscopy (XRF), X-ray Diffractometer (XRD), Fourier Transform Infrared Spectrometer (FT-IR), nitrogen adsorption (Brunauer-Emmett-Teller - BET) and Temperature Programmed Desorption of ammonia (NH₃-TPD). The parameters studied in this work are amount of aluminium, reaction temperature and hydrogen peroxide per toluene molar ratios. This study found that the addition of Al into TS-1 does not destroy the structure of TS-1. Furthermore, addition of Al promotes the formation of benzaldehyde. All modified catalysts yield benzaldehyde as the major product with a small amount of o-cresol and p-cresol as by-products. The experimental results also show that increasing of the reaction temperature increases the reaction rate. However, the conversion of H₂O₂ may increase only slightly or decreases in some cases. In addition, increasing molar ratio of H₂O₂ per toluene increases benzaldehyde formation.

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ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

CONTENTS

	Page
ABSTRACT (THAI)	iv
ABSTRACT (ENGLISH)	v
ACKNOWLEDGEMENTS	vi
CONTENTS	vii
LIST OF TABLES	x
LIST OF FIGURES	xii
CHAPTER	
I INTRODUCTION	1
II THOERY AND LITERATUER REVIEWED	5
2.1 Titanium Silicalite –1.....	5
2.1.1 Application of TS-1.....	6
2.2 Benzaldehyde.....	7
2.2.1 Production.....	7
2.2.2 Hydrolysis of benzalchloride.....	7
2.2.3 Oxidation of toluene.....	8
2.3 Mechanism for the formation of benzaldehyde.....	9
2.4 Oxidation of toluene.....	10
2.5 Toluene solubility in water.....	11
2.6 Related literatures.....	12
2.7 Comments on previous works.....	15
III EXPERIMENTAL	16
3.1 Catalyst preparation.....	16
3.2 Catalyst characterization.....	20
3.2.1 X-ray fluorescence spectroscopy (XRF.).....	20
3.2.2 X-ray diffraction (XRD).....	20
3.2.3 Fourier-transform infrared spectroscope (FT-IR.).....	21
3.2.5 Brunaur-Emmett (BET surface area).....	21

3.2.6 Temperature Programmed Desorption of ammonia (NH ₃ -TPD).....	21
3.3 Reaction study in oxidation of toluene.....	22
3.3.1 Chemicals.....	22
3.3.2 Reaction procedure.....	22
3.4 Calculation of H ₂ O ₂ convert to product, productivity and %selectivity.....	24
IV RESULTS AND DISCUSSION.....	26
4.1 Characterization of catalysts.....	26
4.1.1 Catalyst composition (XRF).....	26
4.1.2 Crystal structure (XRD).....	27
4.1.3 Fourier Transform Infrared (FT-IR).....	28
4.1.4 Surface Area (BET).....	30
4.1.5 Temperature Programmed Desorption of ammonia (NH ₃ -TPD).....	30
4.2 The catalytic reaction.....	35
4.2.1 The effect of reaction temperature.....	35
4.2.2 The effect to molar ratio of reactant (H ₂ O ₂ : Toluene).....	43
4.3 Proposed mechanism for the formation of benzaldehyde and cresols.....	47
4.3.1 Proposed mechanism for the formation of cresols.....	47
4.3.2 Proposed mechanism for the formation of benzaldehyde.....	50
V CONCLUSIONS AND RECOMMENDATIONS.....	52
5.1 Conclusions.....	52
5.2 Recommendations for further study.....	53
REFERENCES.....	54
APPENDICES.....	56
Appendix A Calculation for catalyst preparation.....	57
Appendix B Calculation of metal quantity.....	59
Appendix C Data of calculation of acid site.....	63

	Page
Appendix D Calibration curves.....	66
Appendix E Data of experiments.....	68
Appendix F Material safety data sheet.....	76
VITA	93



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF TABLES

TABLE	Page
3.1 Chemicals used in the catalyst preparation.....	16
3.2 Reagents used for the preparation of TS-1, Al-TS-1: Si/Ti = 50, Si/Al = 50, 100, 150 and 200.....	17
3.3 The chemicals used for the reaction study.....	22
3.4 Operating conditions for gas chromatograph.....	23
4.1 The chemical compositions of TS-1 and Al-TS-1.....	26
4.2 The surface area of TS-1 and Al-TS-1.....	30
4.3 The strength and amount of the acid site of the catalysts.....	31
4.4 Reaction conditions for TS-1 and Al-TS-1.....	36
B1 Data of TS-1 from XRF technique.....	59
B2 Calculated composition of TS-1.....	60
B3 Calculated composition of Al-TS-1 (206).....	61
B4 Calculated composition of Al-TS-1 (166).....	61
B5 Calculated composition of Al-TS-1 (127).....	62
B6 Calculated composition of Al-TS-1 (69).....	62
C1 Data from fityk programme.....	63
E1 Data of Figure 4.8.....	68
E2 Data of Figure 4.9.....	68
E3 Data of Figure 4.10.....	69
E4 Data of Figure 4.11.....	69
E5 Data of Figure 4.12.....	70
E6 Data of Figure 4.13.....	70
E7 Data of Figure 4.14.....	71
E8 Data of Figure 4.15.....	71
E9 Data of Figure 4.16.....	72
E10 Data of Figure 4.17.....	72
E11 Data of Figure 4.18.....	73
E12 Data of Figure 4.19.....	73

TABLE	Page
--------------	-------------

	xi
E13 Data of Figure 4.20.....	74
E14 Data of Figure 4.21.....	74
E15 Data of Figure 4.22.....	75



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF FIGURES

FIGURE	Page
1.1 The synthesis route of benzaldehyde from toluene.....	2
2.1 MFI structure.....	5
2.2 Hydrolysis of benzal chloride.....	7
2.3 The oxidation of toluene.....	8
2.4 The mechanisms of benzaldehyde formation by hydroxyl free radical.....	10
2.5 Oxidation of toluene over TS-1 catalyst.....	11
2.6 Temperature influence on toluene solubility in water and toluene partitioning from gasoline into water at 50 bar.....	12
3.1 The preparation procedure of Al-TS-1 by rapid crystallization method.....	18
3.2 Schematic diagram of the reaction.....	24
4.1 XRD patterns of TS-1 and Al-TS-1.....	28
4.2 FT-IR spectra of TS-1 and Al-TS-1 catalysts.....	29
4.3 NH ₃ -TPD of TS-1 catalyst.....	32
4.4 NH ₃ -TPD of Al-TS-1 (206) catalyst.....	32
4.5 NH ₃ -TPD of Al-TS-1 (166) catalyst.....	33
4.6 NH ₃ -TPD of Al-TS-1 (127) catalyst.....	33
4.7 NH ₃ -TPD of Al-TS-1 (69) catalyst.....	34
4.8 %H ₂ O ₂ convert to product of molar ratio H ₂ O ₂ : toluene = 1:1.....	37
4.9 Productivity of molar ratio H ₂ O ₂ : toluene = 1:1.....	38
4.10 %Selectivity of molar ratio H ₂ O ₂ : toluene = 1:1.....	39
4.11 %H ₂ O ₂ convert to product of molar ratio H ₂ O ₂ : toluene = 1:1.....	40
4.12 Productivity of molar ratio H ₂ O ₂ : toluene = 1:1.....	40
4.13 %Selectivity of molar ratio H ₂ O ₂ : toluene = 1:1.....	41
4.14 %H ₂ O ₂ convert to product of molar ratio H ₂ O ₂ : toluene = 2:1.....	41
4.15 Productivity of molar ratio H ₂ O ₂ : toluene = 2:1.....	42
4.16 %Selectivity of molar ratio H ₂ O ₂ : toluene = 2:1.....	42
4.17 %H ₂ O ₂ convert to product at 110 °C.....	43
4.18 Productivity at 110 °C.....	44
FIGURE	Page

	xiii
4.19 %Selectivity at 110 °C.....	44
4.20 %H ₂ O ₂ convert to product at 120 °C.....	45
4.21 Productivity at 120 °C.....	46
4.22 %Selectivity at 120 °C.....	46
4.23 The oxidation of toluene at the side chain and benzene ring.....	47
4.24 The mechanism of cresol in the oxidation of toluene (a) o-cresol and (b) p-cresol.....	49
C1 The calibration curve of ammonia.....	64
D1 The calibration curve of benzaldehyde.....	66
D2 The calibration curve of o-cresol.....	67
D3 The calibration curve of p-cresol.....	67



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER I

INTRODUCTION

Benzaldehyde (C_6H_5COH) is a chemical compound consisting of a benzene ring with an aldehyde substituent. This compound is a colorless liquid and almond-like smell. It is widely used in commercial food flavorant, dyestuff, perfumery, and pharmaceutical industries. Purified benzaldehyde is used as an intermediate in closed systems and used as a solvent oil, resins, some cellulose ethers, cellulose acetate and nitrate. In the latter industry it is used for the manufacture of intermediates for chloramphenicol, analgin, ephedrine, and ampicillin.

The oldest benzaldehyde is produced by many processes such as the liquid phase oxidation of toluene, vapor phase oxidation of toluene and chlorination of toluene. The liquid phase oxidation and the vapor phase oxidation of toluene begin from reacting toluene with oxygen. The main by product, more than 70%, of the vapour phase oxidation is CO_2 . The difference between the gas phase and the liquid phase is the reaction temperature. Another disadvantage of the liquid phase oxidation of toluene and vapor phase oxidation of toluene is the use of hazardous multi step and the use of a large amount of energy in the separation process and give by product that is dissatisfied which is pass through several separation steps.

The chlorination of toluene is another way to produce benzaldehyde. First, the toluene reacts with chlorine in the presence of light to gain benzal chloride and benzyl chloride and then hydrolyses benzal chloride to obtain benzaldehyde with by product. The disadvantages of this route are (i) the reaction consists of two steps, (ii) the use of light to activate the chlorination reaction, and (iii) the formation of by product.

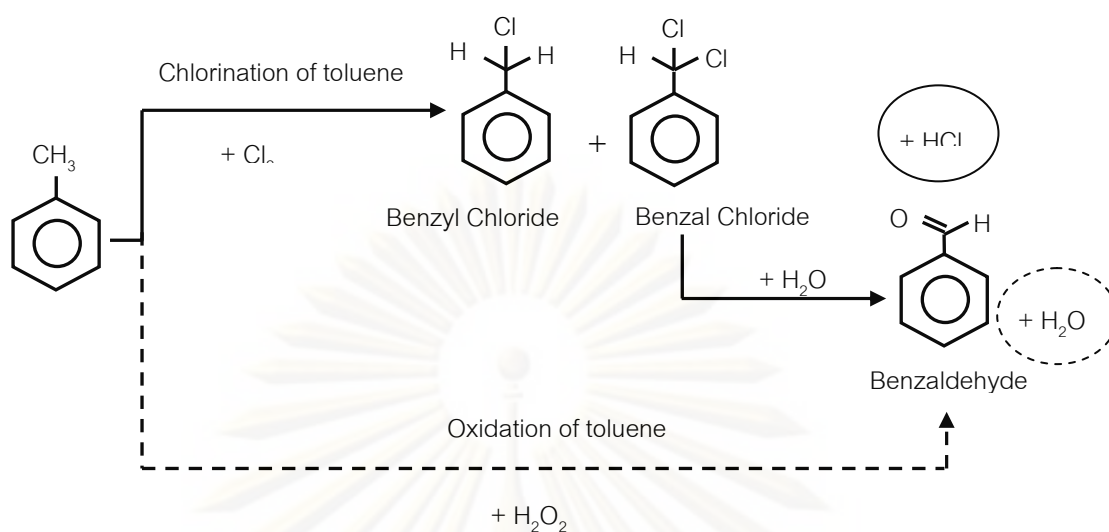


Figure 1.1 The synthesis route of benzaldehyde from toluene.

The synthesis of titanium sicalite-1 (commonly known in the name TS-1) was firstly reported by Taramasso et al. in 1983. TS-1 is a silica rich molecular sieve with MFI structure in which isolated titanium species in the zeolite framework function as catalytic sites. Moreover, TS-1 has unique catalytic properties, being effective in the oxidation of a variety of organic compounds at low temperature, using diluted hydrogen peroxide as an oxidant such as the conversions of ammonia to hydroxylamine, of secondary alcohols to ketones and of secondary amines to dialkylhydroxylamines or reactions such as the phenol hydroxylation, the olefin epoxidation, the ketone ammoximation and also sulfide and disulfide oxidation. For these reasons TS-1 has become one of the most relevant oxidation industrial catalysts.

Harnvanich (2008) studied the oxidation of toluene by using H_2O_2 as the oxidant over TS-1 and TS-1 modified with different amount of Al (Al-TS-1). The reaction was carried out at reaction temperatures $70\text{ }^\circ\text{C}$ and $90\text{ }^\circ\text{C}$. The results showed that all modified catalysts yield benzaldehyde as the major product with o-cresol and p-cresol as by-products in a much less amount. Furthermore, the conversion of H_2O_2 and benzaldehyde selectivity increased with increasing the reaction temperature.

Another benefit from increasing temperature is more amount of toluene can be dissolved in water (Valtz et al. (2007) and Yang et al. (1997)). Therefore, the opportunity which toluene, H_2O_2 and catalyst contact together and convert into products is increased.

Because no researcher has run the reaction higher than the temperature of the minimum boiling point of the reactant or the solvent. But these boiling points can be increased by increasing the pressure above the liquid surface. Therefore, in this work, the reaction at temperature over boiling point of reactant or solvent by increasing the system pressure is interested. It is expected that further increase of the reaction temperature not only increases the conversion of H_2O_2 but also the selectivity of benzaldehyde.

This research studies the performances of TS-1 and TS-1 which is modified with Al (Al-TS-1) catalysts on the toluene oxidation reaction by using H_2O_2 as the oxidizing agent in liquid phase condition at elevated temperature. The research has scope following as:

1. Synthesizing TS-1 and metal modified TS-1 (Al-TS-1) catalysts which have 50 for Si/Ti and 50, 100, 150 and 200 for Si/Al using incorporation technique to introduce second metal during hydrothermal synthesis.

2. The synthesized catalysts 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 Diffractometer (XRD) to determine the structure of catalysts.
- Fourier Transform Infrared Spectrometer (FT-IR) to determine the incorporation of Ti atoms as a framework element.
- Nitrogen adsorption based on Brunauer-Emmett-Teller method (BET) to determine surface area pore size and pore volume.
- Temperature Programmed Desorption of ammonia (NH_3 -TPD) to determine the strong acid and weak acid sites of the catalyst.

3. Investigate catalytic behavior of synthesized catalysts are evaluated by oxidation of toluene using H_2O_2 as an oxidant with differences temperature reaction.

The present thesis is organized as follows:

Chapter I presents the background and scopes of the research.

Chapter II reviews the theory of this research and literature on the catalytic activity of metal modified TS-1 catalysts in the oxidation of aromatics reaction and comments on previous works.

Chapter III consists of catalyst preparation procedure, techniques used in the characterization of catalysts and catalytic activity evaluation in the toluene oxidation by H_2O_2 at elevated temperature.

Chapter IV presents the experimental results of the characterization of catalysts, and the oxidation of toluene reactions over the investigated catalysts, including an expanded discussion.

Chapter V contains the overall conclusions emerging from this research and some recommendations for future work.

Finally, the sample of calculation of catalyst preparation, calibration curves from area to mole of reaction products and data of the experiments which have emerged from this study research are included in appendices at the end of this thesis.

CHAPTER II

THEORY AND LITERATURE REVIEWED

2.1 Titanium silicalite – 1

Titanium silicalite is an interesting material obtained by isomorphic substitution of trivalent metals or tetravalent metals in the framework of crystalline aluminosilicates or silicates. Titanium silicalites with MFI (TS-1) structures have been used in several oxidation reactions with H_2O_2 as the oxidizing agent.

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 built up by 5-1 secondary building units (SBU; the smallest number of TO_4 units, where T is Si from which zeolite topology is built) which are link together to form chain in figure 2.1 and the inter connection 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 - 5.3 Å) and intersecting straight 10 - ring channels (Tosheva (1999)).

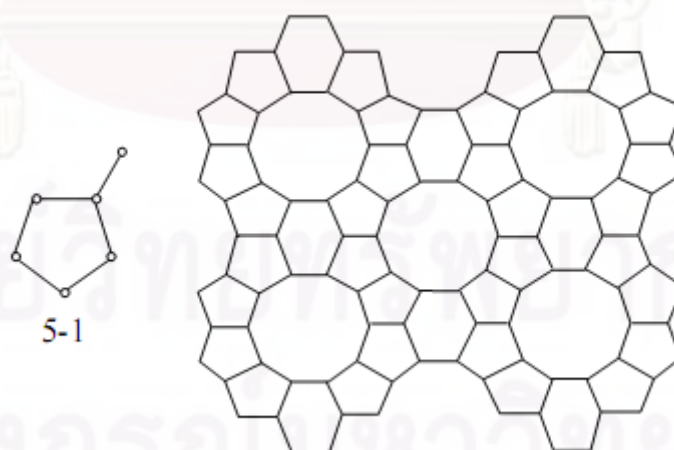


Figure 2.1 MFI structure (Tosheva (1997)).

Titanium has a stable valence of 4 and in an oxidizing medium it is very likely that this valence is maintained. An examination of the chemistry of Ti^{4+} compounds immediately shows that Ti^{4+} has a strong tendency to assume a high coordination number: with oxygen, six groups in octahedral coordination form a stable and very frequently observed configuration, but to do this Ti^{4+} must have near neighbours capable of increasing their coordination number to satisfy at the same time titanium valency of four and coordination of six. When bulky groups are linked to Ti^{4+} , tetrahedral coordination is also observed. Coordination of seven in a pentagonal pyramidal arrangement like in peroxy compounds and of eight like in $Ti(NO_3)_4$ are also observed.

2.1.1 Application of TS-1

Since its discovery in early 80's TS-1 has been studied mainly, as oxidation catalyst for a variety of reactions in presence of aqueous H_2O_2 as oxidant. Examples of TS-1 as oxidation catalysts are manifested in the following reactions,

- Oxyfunctionalization of alkanes
- Hydroxylation of aromatics
- Epoxidation of alkenes
- Oxidation of alcohols
- Oxidation of ethers
- Ammoximation of carbonyl compounds
- Oxidation of amines
- In Bayer-Villiger oxidation to form lactones

Other than its use as oxidation catalyst, it is also used in C-C bond formation (Mukherjee (2000)).

2.2 Benzaldehyde

Benzaldehyde is the simplest and industrially the most important aromatic aldehyde. It exists in nature, occurring in combined and uncombined forms in many plants. The best known natural source of benzaldehyde is amygdalin, in which it exists in a combined form as a glycoside and which is present in bitter almonds. The odor of bitter almonds arises from a small amount of benzaldehyde formed by hydrolysis of amygdalin. Owing to its occurrence in bitter almonds, the aldehyde was formerly referred to as "bitter almond oil". Benzaldehyde is also the main constituent of the essential oils obtained by pressing the kernels of peaches, cherries, apricots, and other fruits.

2.2.1 Production

Benzaldehyde is produced principally by the hydrolysis of benzal chloride or the partial oxidation of toluene. There are various other manufacturing processes, but at present they have no industrial importance.

2.2.2 Hydrolysis of benzal chloride

The hydrolysis of benzal chloride, which is readily obtainable by side-chain chlorination of toluene, is among the oldest industrial processes for the production of benzaldehyde. It can be carried out either in an alkaline or in an acidic medium.

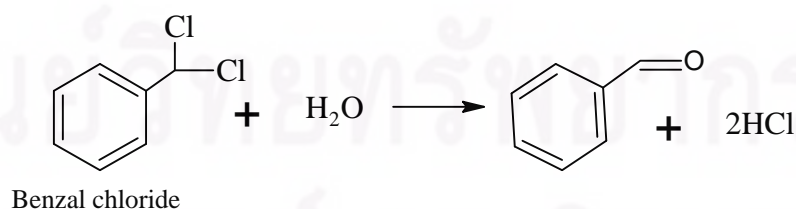


Figure 2.2 Hydrolysis of benzal chloride.

Benzal chloride can also be converted into benzaldehyde by boiling with aqueous solutions of hexamethylenetetramine. Because benzyl chloride also reacts with hexamethylenetetramine to give benzaldehyde, industrial mixture of benzyl chloride and benzal chloride can be used to form benzaldehyde in this way.

The acid hydrolysis of benzal chloride is carried out in the presence of acids and with metal salts as a catalyst. It gives very high yields of benzaldehyde (more than 90%).

The hydrolysis of benzal chloride was at one time commonly carried out in the presence of concentrated sulfuric acid. This process has disadvantage that large amounts of dilute sulfuric acid are formed as a waste product.

2.2.3 Oxidation of toluene

The partial oxidation of toluene with oxygen to give benzaldehyde can be carried out in either the gas phase or liquid phase. Benzaldehyde itself is easily further oxidized to benzoic acid and other products. Conditions must therefore be carefully chosen to favor only partial oxidation.

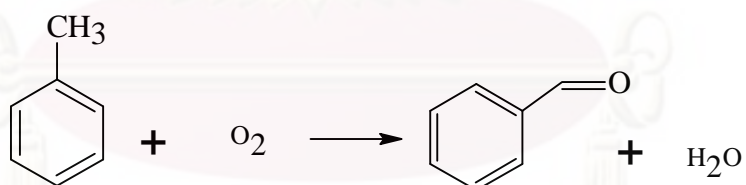


Figure 2.3 The oxidation of toluene.

In the gas phase, the oxidation is carried out by passing toluene vapor, together with oxygen in a gaseous mixture such as air, through a catalyst bed in a tube bundle or fluidized-bed reactor at a temperature of 250 - 650 °C. The reaction is highly exothermic, and effective cooling is necessary.

More important than gas-phase oxidation for the production of benzaldehyde is the oxidation of toluene in the liquid phase by oxygen in the form air or other gaseous mixtures. This is carried out at 250 °C.

Those processes in which toluene is oxidized with other agents such as manganese dioxide in sulfuric acid, sodium persulfate, chromium (VI) oxide in acetic anhydride or chromyl chloride cause waste water disposal problems and are without industrial importance.

2.3 Mechanism for the formation of benzaldehyde

Mechanism for the formation of benzaldehyde is shown in figure 2.4 below. The mechanism in Figure 2.4 follows the generally accepted free radical substitution of halogen. The only difference is halogen atom ($X\bullet$) is replaced by hydroxyl free radical ($OH\bullet$). The initiating step is the breaking of O-O bond of the H_2O_2 into two hydroxyl free radicals (step 1 in Figure 2.4). The oxygen atom of the hydroxyl free radical is very reactive because it has an incomplete valance shell. When the hydroxyl free radical collides with the methyl group of toluene molecule, it will abstract a hydrogen atom from the methyl group with results in the formation of benzyl alcohol. Due to the nature of primary alcohol which can be easily oxidized, the benzyl alcohol forms is then rapidly oxidized by H_2O_2 to benzaldehyde (step 2 in Figure 2.4) (Kasemsiri (2007)).

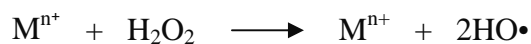
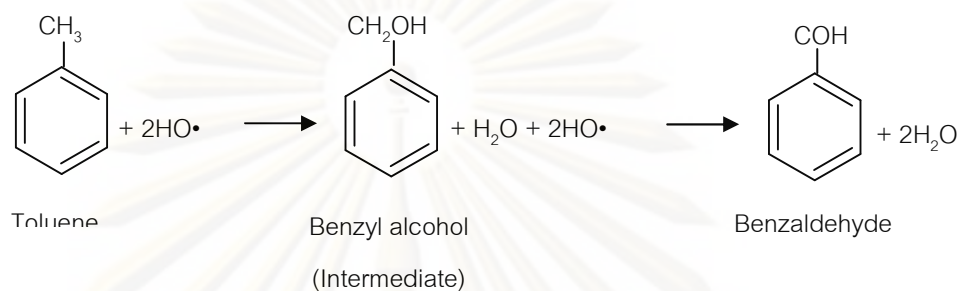
Step 1**Step 2**

Figure 2.4 The mechanisms of benzaldehyde formation by hydroxyl free radical.

2.4 Oxidation of toluene

Purposal that the direct oxidation of toluene in an attractive route for the preparation of benzaldehyde is showed in Figure 2.5, Although TS-1 has been used as catalyst for toluene oxidation in the presence of dilute H₂O₂ and an organic solvent by some workers (Wongbunrod (2008)). In the case of toluene there are two oxidation sites. One is primary carbon atom of the side chain methyl group and the other one is the ring.

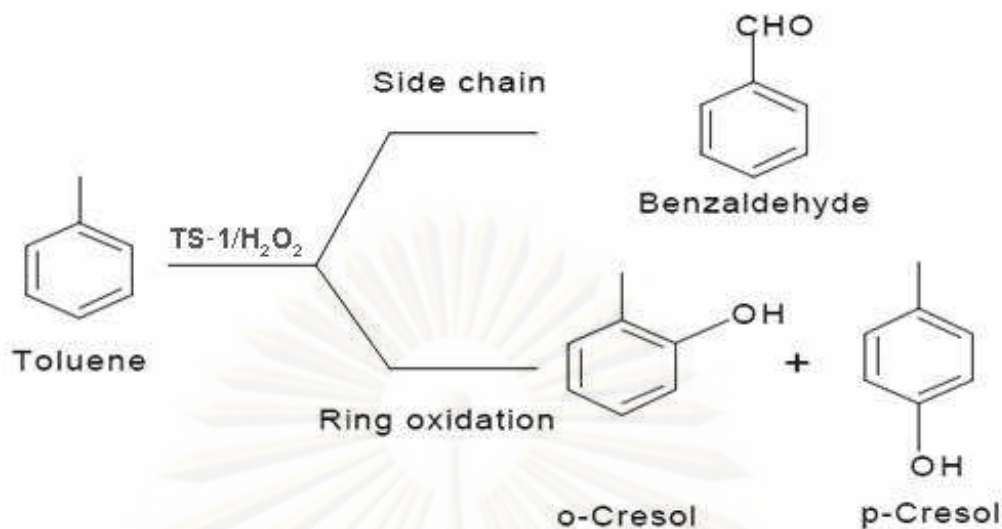


Figure 2.5 Oxidation of toluene over TS-1 catalyst (Wongbunrod (2008)).

2.5 Toluene solubility in water

Although toluene is a nonpolar liquid, in reality it can dissolve into water at an amount.

The solubility of toluene in water at different temperature is showed in Figure 2.6. From this figure, one can obviously see that toluene solubility in water increases rapidly when increasing the water temperature (The boiling points of water and toluene can be increased by increasing the pressure of the system.). Therefore, increasing the temperature of the reactor system will result in higher amount of toluene in the aqueous phase. Thus providing more opportunity for toluene, H_2O_2 and catalyst to contact altogether and convert into products.

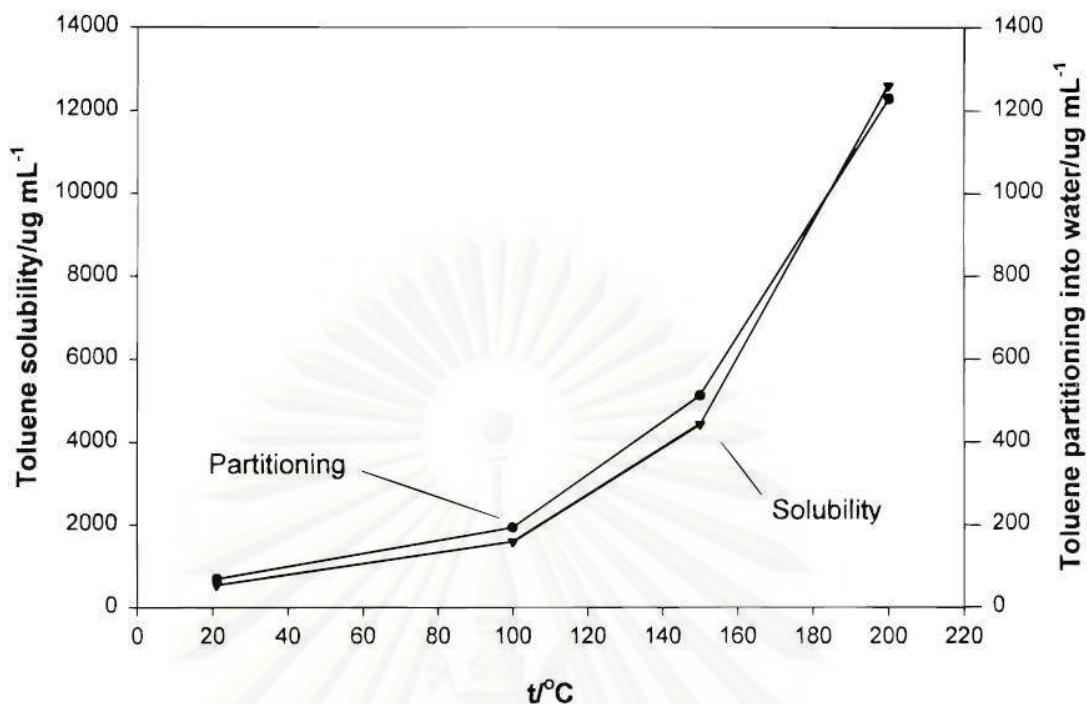


Figure 2.6 Temperature influence on toluene solubility in water and toluene partitioning from gasoline into water at 50 bar (Valtz et al. (2007)).

2.6 Related literatures

Wang and Guo (1999) studied the synthesis of titanium silicalite-1 by hydrothermal crystallization synthesis method (hydrothermal crystallization was carried out at 150 - 180 °C for 2 - 5 days). Their results indicated that titanium had been incorporated into the framework. The addition of seeds decreased the crystal size. They found a possible way of decreasing the cost of TS-1 by using tetrapropylammonium bromide, TPABr (usually free from alkali metal cations) to replace tetrapropylammonium hydroxide, TPAOH. Their IR spectra had a characteristic peak at about 960 cm⁻¹, which indicated that titanium has been incorporated into the framework of zeolite.

Li et al. (2001) synthesized titanium silicalite TS-1 by hydrothermal method. It has been observed that several kinds of titanium species may exist in titanium silicalite. The form that titanium atoms incorporate into the framework of titanium silicalite synthesized using tetrapropylammonium bromide (TPABr) were found to

different from that using the classical method (the classical method used tetrapropylammonium hydroxide, TPAOH as the template). In order to reduce the cost of TS-1, they suggested that TPABr was suggested the template to replace tetrapropylammonium hydroxide (TPAOH), the symmetry of titanium silicalite was found to change from monoclinic to orthorhombic with the increased of titanium content in both methods. They also suggested that the Ti-O_2^- originated from framework titanium and H_2O_2 had the moderate stability and might be active site in oxidation reaction. TS-1 synthesized using TPABr did not contain anatase, but contained a kind of partly condensed titanium species with six-fold coordination. The titanium was at 270 - 280 nm in UV-VIS spectra and form in Ti-O_2^- . But, this kind of Ti-O_2^- was found to be very stable and cannot be catalytic active site. Therefore, they suggested that so, the six-fold coordination titanium species may be inactive in both the oxidation reaction and the decomposition of H_2O_2 .

Pirutko et al. (2001) synthesized the titanosilicalite TS-1 samples modified by Al, V, Cr, Fe, Co, and Ru by hydrothermal technique (held at a constant temperature of 175 °C for 96 h) and tested in the oxidation of benzene to phenol by N_2O . XRD analysis demonstrated that all of their samples had the MFI crystal structure. IR spectroscopy were used to prove that the Ti has entered the silicalite lattice, due to the observation that an additional band typical for tetrahedral group $\text{Ti}(\text{OSi})_4$ appeared in the silicalite spectrum at 960 cm^{-1} . Al MAS NMR spectrum of Al-TS-1 also showed a peak at 55 ppm, typical for Al atoms in a tetrahedral position which indicated that the Al entered the crystal lattice of TS-1 were used to introduction Fe into the TS-1 that could catalyze the oxidation of benzene to phenol with high activity and selectivity. Other metals were shown to be inert.

Shenchunthichai (2006) studied the catalytic activity of titanium silicalite-1 (TS-1) catalysts modified by Fe Al Co and V were synthesized, characterized and tested in the hydroxylation of benzene by H_2O_2 and the effects of pretreatment with nitric acid aqueous solution on the catalytic activity of catalysts. The results of the reaction showed that the Fe Al Co and V incorporated in TS-1 framework promoted the catalytic activity higher than TS-1. After the catalysts were pretreated by nitric acid aqueous solution, the framework structure of catalyst was not destroyed and titanium in the framework was not removed. The activity of the pretreated catalysts

was found to be improved. The catalytic activity of the investigated catalyst was reported in the following order $\text{Co-TS-1} > \text{V-TS-1} > \text{Fe-TS-1} > \text{Al-TS-1} > \text{TS-1}$.

Kasemsiri (2007) studied the synthesis of TS-1 and modified TS-1 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 have 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 followed the order: $\text{Fe-TS-1} (10.01\%) > \text{Al-TS-1} (5.39\%) > \text{TS-1} (1.09\%) > \text{Co-TS-1} (0.85\%) > \text{V-TS-1} (0.34\%)$ and the selectivity of product observed followed the sequence: $\text{TS-1} > \text{Co-TS-1} > \text{V-TS-1} > \text{Al-TS-1} > \text{Fe-TS-1}$.

Harnvanich (2008) studied the synthesis of TS-1 and modified TS-1 with different amount of Al (Al-TS-1) by hydrothermal method. The reaction is carried out at reaction temperature 70 °C and 90 °C, and toluene per hydrogen peroxide molar ratios 1:1 and 2:1. The catalytic activity testing found that all modified catalysts yield benzaldehyde as the major products with o-cresol and p-cresol as by products. The results show that, increasing of reaction temperature increases the reaction rate, and increases H_2O_2 conversion but will also increase cresol selectivity.

2.7 Comments on previous works

Despite the fact that the hydroxylation of benzene by H_2O_2 to phenol is still widely studied, the reaction between H_2O_2 and toluene is still limited to some groups. Both reactions, however, share the same problem that is how to mixed the solid, the polar liquid and the non polar liquid altogether.

Attempts have been made by introducing organic solvents which can homogenize the aqueous and the hydrocarbon phases together. A major disadvantage to this technique is the solvent has to be recovered and reused. An alternative method is to raise the temperature of the reaction system. It is known that as the temperature of water raises up, more hydrocarbons can dissolve in to water phase.

An alternative method is to raise the temperature of the reaction system. It is known that as the temperature of water raises up, more hydrocarbon can dissolve in to water phase.

This research is, therefore, set up by trying to operate the reactor at temperatures higher than previously used. This is achieved by raising the operating pressure of system. Details and outcomes of this research can be read in subsequent chapters.

CHAPTER III

EXPERIMENTAL

The experimental in this chapter is divided into three major parts: (1) catalyst preparation, (2) catalyst characterization and (3) reaction study in oxidation of toluene. The chemicals, apparatus and procedures for catalyst preparation are explained in section 3.1. The composition, structure, surface properties and acidity of the catalyst are characterized by various techniques such as XRF, BET, XRD, FT-IR and NH_3 -TPD are discussed in section 3.2. The details of the reaction study are explained in section 3.3.

3.1 Catalyst preparation

The preparation of TS-1 and Al-TS-1 catalysts uses the incorporation method. The same amount of aluminium nitrate nanohydrate is added in both gel solution and decantation solution. All chemicals use in this preparation procedure of TS-1 and Al-TS-1 catalysts are 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 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
Cobalt (II) nitrate hexahydrate	Analytical	Aldrich

Table 3.2 Reagents use for the preparation of TS-1, Al-TS-1: Si/Ti = 50, Si/Al = 50, 100, 150 and 200.

Solution for the gel preparation		Solution for decant-solution preparation	
<u>Solution A1</u>		<u>Solution A2</u>	
Ti[O(CH ₂) ₃ CH ₃] ₄	2.2970 g	Ti[O(CH ₂) ₃ CH 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 ₂ O, Si/Al = 200	0.61 g	Al(NO ₃) ₃ .9H ₂ O, Si/Al = 200	0.61 g
Al(NO ₃) ₃ .9H ₂ O, Si/Al = 150	0.82 g	Al(NO ₃) ₃ .9H ₂ O, Si/Al = 150	0.82 g
Al(NO ₃) ₃ .9H ₂ O, Si/Al = 100	1.23 g	Al(NO ₃) ₃ .9H ₂ O, Si/Al = 100	1.23 g
Al(NO ₃) ₃ .9H ₂ O, Si/Al = 50	2.46 g	Al(NO ₃) ₃ .9H ₂ O, Si/Al = 50	2.46 g
De-ionized water	60 ml	H ₂ SO ₄ (conc.)	3.4 ml
H ₂ SO ₄ (conc.)	3.4 ml		
<u>Solution B1</u>		<u>Solution B2</u>	
Sodium silicate	69 g	Sodium silicate	69 g
De-ionized water	45 ml	De-ionized water	45 ml
<u>Solution C1</u>		<u>Solution C2</u>	
TPABr	2.16 g	NaCl	26.27 g
NaCl	40.59 g	De-ionized water	104 ml
NaOH	2.39 g		
De-ionized water	208 ml		
H ₂ SO ₄ (conc.)	1.55 ml		

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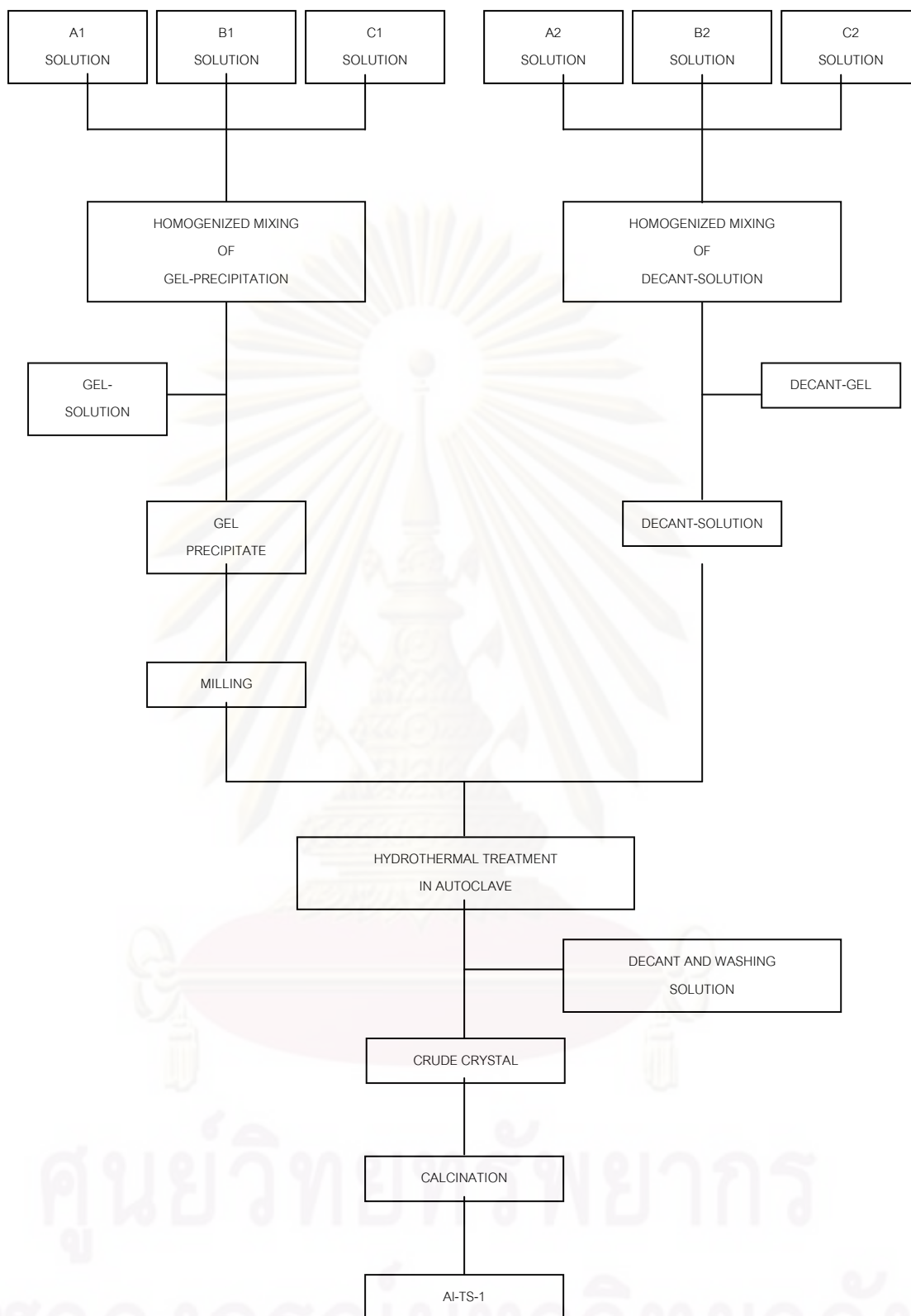


Figure 3.1 The preparation procedure of Al-TS-1 by rapid crystallization method.

The source of metals for preparation of decantation and gel solutions are $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ for Al, $\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$ for Ti and sodium silicate for Si, respectively. TPABr (Tetra-n-propyl ammonium bromide $[(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{N}]\text{Br}$) is used as organic template. The atomic ratio of Silicon/Titanium is 50 and Silicon/Metal is set at 50, 100, 150 and 200. The preparation of supernatant liquid is separated from the gel, which is important for preparing the uniform crystals. The detail procedures are as follows: firstly, a gel mixture is prepared by adding solution A-1 and solution B-1 into solution C-1 drop wise with vigorous stirring using a magnetic stirrer at room temperature. The pH of the gel mixture is maintained within the range 9-11 because this pH range is suitable for precipitation. H_2SO_4 (conc.) or KOH solution are used to adjust pH of the gel mixture to an appropriate level if it is necessary. The gel mixture is separated from the supernatant liquid by a centrifuge. The precipitated gel mixture is milled for totally 1 hour. The milling is done for 15 min and then the supernatant solution is removed by centrifugal separation before the hydrothermal treatment in order to obtain the uniform, fine crystals. The milling procedure is as follows: mill 15 min \rightarrow centrifuge (to remove liquid out) 15 min \rightarrow mill 15 min \rightarrow centrifuge 15 min \rightarrow mill 30 min \rightarrow centrifuge 15 min.

Secondly, a decantation solution is prepared by adding solution A-2 and solution B-2 into solution C-2, same as for the preparation of gel mixture. The supernatant liquids from A-2, B-2 and C-2 are mixed together with the milled gel mixture. However, before mixing, the pH of solution was maintained between 9-11. The colorless supernatant liquid is separated from the mixture by centrifugation.

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

The obtained product crystals are washed with de-ionized water decreased pH from about 12 to 7 by centrifugation in order to remove chloride out of the crystals. Then the crystals are dried in an oven at 110 °C for at least 24 h. The dry crystals are calcined in an air stream at 550 °C and held at that temperature for 7 h, by heating them from room temperature to 550 °C at a heating rate at 10 °C/min. The calcined crystals are finally cool down to room temperature.

TS-1 and Al-TS-1 are placed into a round bottom flask then 5 M of HNO₃ aqueous solution is added. After reflux at 80 °C for 3 h, the pretreated catalyst is filtered, washed with distilled water until pH 7, dried at 110 °C and calcined at 540 °C for 7 h in static air.

3.2 Catalyst characterization

3.2.1 X-Ray Fluorescence Spectrometer (XRF)

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

3.2.2 X-Ray Diffraction (XRD)

The crystallinity and X-ray diffraction patterns of the catalysts are performed by an X-ray diffractometer SIEMENS D5000 connected with a computer with Diffract ZT version 3.3 program for fully control of XRD analyzer. The experiments are carried out by using Cu K α radiation with Ni filter. Scans are performed over the 2 θ ranges from 6 ° to 30 ° with step size 0.04 °/sec.

3.2.3 Fourier Transform Infrared (FT-IR)

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

3.2.4 BET surface area measurement

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

3.2.5 Temperature Programmed Desorption of ammonia (NH_3 -TPD)

Temperature programmed desorption of ammonia (NH_3 -TPD) is used to determine the acid properties of catalysts. NH_3 -TPD is carried out using a flow apparatus. The catalyst sample (0.1 g) is treated at 550 °C in helium flow for 1 h and then saturated with 15 % NH_3 /He mixture after cooling to 80 °C. After purging with helium at 80 °C for 1 h to remove weakly physisorbed NH_3 , the sample is heated to 550 °C at the rate of 10 °C/min in a helium flow of 50 ml/min. The amount of acid sites on the catalyst surface is calculated from the desorption amount of NH_3 . It is determined by measuring the areas of the desorption profiles obtained from the Micromeritics Chemisorb 2750 analyzer.

The deconvolution of NH_3 -TPD peak is carried out with the “fityk” curve fitting programme. The peaks are assumed to be Gaussian with showiness shape (using parameter ‘SplitGaussian’ in the programme).

3.3 Reaction study in oxidation of toluene

3.3.1 Chemicals

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

Table 3.3 The chemicals use for the reaction study.

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

3.3.2 Reaction procedure

The Oxidation of toluene with molar ratio of reactant (H_2O_2 : toluene) is 1:1 and 2:1 using TS-1 and Al-TS-1 as a catalyst is carried out in a stainless steel reactor. The procedures are described in the detail below.

1. Catalyst 1 g, magnetic bar, water 50 ml (for dispersion of the catalyst) and toluene 1.1 ml are added into the reactor and adjust the pressure to 2 bars by nitrogen gas.
2. Heat up the reactor by raising the oil bath temperature to 90 °C for 1 h to drive out gases in pores of the catalyst.
3. If the reaction temperature is 70 °C, let the reactor cools down to 70 °C before starting the reaction. the reaction temperature is 110 °C or 120 °C, pressurizes the reactor with nitrogen gas to 2 barg. Then, heats the reactor to the desired reaction temperature before starting the reaction. The final pressure in the reactor depends on the reaction temperature, i.e. 4 barg at 70 °C, 5 barg at 110 °C and 5.5 barg at 120 °C.

4. Start the reaction by injecting hydrogen peroxide 30 wt% 1 ml (for H₂O₂ to toluene molar ratio equals to 1:1) or 2 ml (for H₂O₂ to toluene molar ratio equals to 2:1) in a single injection into the reactor.

5. After 30 min, the mixture is immediately cooled down by removing the reactor from the oil bath and put into an ice bath in order to stop the reaction. After the reactor is cooled down, 50 ml of ethanol is injected into the reactor to homogenize the liquid mixture in the reactor.

6. The catalyst particle is separated from the homogeneous mixture by using the micro-centrifuge.

7. The liquid product is analyzed by the FID gas chromatography. The operations conditions of the GC are listed in Table 3.4 below. The chromatogram data are converted into mole of products using a calibration curve showed in appendix D.

Table 3.4 Operating conditions for gas chromatograph.

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)	5
Analyzed chemicals	Toluene, Benzaldehyde and Cresol

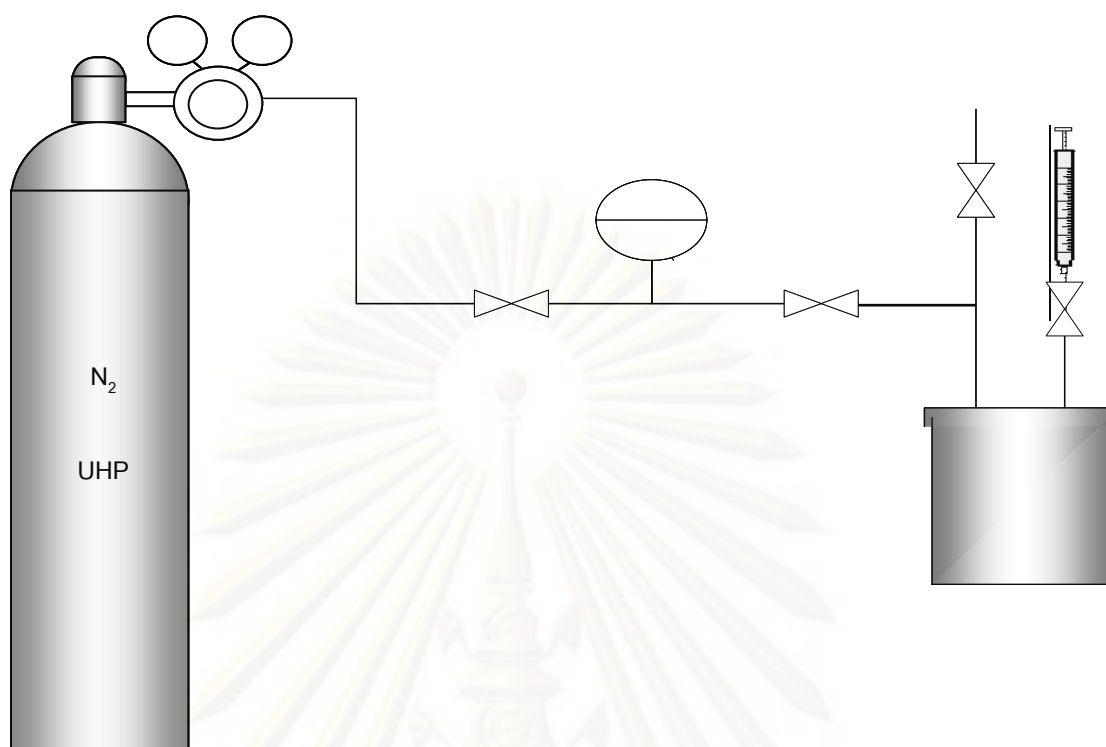


Figure 3.2 Schematic diagram of the reaction.

3.3.3 Calculation of H_2O_2 convert to product, productivity and %selectivity

The equations for calculating percentage of H_2O_2 convert to products, product productivity and selectivity of each product are as follows :

1. Percentage of H_2O_2 convert to product

$$\% \text{H}_2\text{O}_2 \text{ convert to product} = \frac{(2 \times \text{mole of benzaldehyde}) + \text{mole of cresol}}{\text{mole of H}_2\text{O}_2} \times 100$$

2. Productivity of benzaldehyde ($\mu\text{mol}/\text{min}\cdot\text{g}$)

$$\text{Productivity of benzaldehyde} = \frac{\text{mole of benzaldehyde} \times 10^6}{\text{weight catalyst (g)} \times 30}$$

3. %Selectivity of benzaldehyde

$$\% \text{Selectivity of benzaldehyde} = \frac{\text{mole of benzaldehyde}}{\text{overall mole of product}} \times 100$$



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CHAPTER IV

RESULTS AND DISCUSSION

Chapter IV is divided into three parts. The first part, section 4.1, summarizes the physical characters of the synthesized TS-1 and TS-1 modified with aluminium (Al-TS-1) catalysts. The catalyst compositions (measured from XRF technique), crystalline structure (determined from XRD), location of titanium cation (identified from FT-IR) and surface area (measured from BET technique) are reported in section 4.1. Section 4.2 shows and explains the catalytic reaction of TS-1 and Al-TS-1 for the oxidation of toluene. The reaction results are presented in terms of H₂O₂ convert to product, selectivity and productivity of products. The last section, section 4.3, shows proposed mechanism for the formation of benzaldehyde and cresols.

4.1 Characterization of catalysts

4.1.1 Catalyst composition (XRF)

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

Table 4.1 The chemical compositions of TS-1 and Al-TS-1.

Catalysts	%Si	%Ti	%Al	Si/Ti	Si/Al
TS-1	97.48	2.04	0.11	47.8	882
Al-TS-1 (Si/Al = 200)	96.48	1.92	0.47	50.4	206
Al-TS-1 (Si/Al = 150)	97.43	1.76	0.59	55.5	166
Al-TS-1 (Si/Al = 100)	97.35	1.85	0.77	52.7	127
Al-TS-1 (Si/Al = 50)	96.99	1.57	1.41	62.0	69

The results in the table show that the amount of aluminium cation that can be incorporated in the MFI structure increases with the amount of aluminium added into the solutions A1 and A2. Due to Al^{3+} has similar diameter to Si^{4+} , the substitution of Si^{4+} by Al^{3+} should not too difficult. In reality, the technique used to prepare TS-1 in the present work is modified from the rapid crystallization technique developed for the preparation of ZSM-5, an aluminosilicate zeolite.

Since the Si/Al ratios in the synthesized catalysts are different from the ratios used during the synthesis, the name of all the catalysts will be renamed to represent the real Si/Al ratios of the obtained catalysts. From section 4.1.2 forward, Al-TS-1 (Si/Al = 200), Al-TS-1 (Si/Al = 150), Al-TS-1 (Si/Al = 100) and Al-TS-1 (Si/Al = 50) will be named Al-TS-1 (206), Al-TS-1 (166), Al-TS-1 (127) and Al-TS-1 (66) respectively (the numbers “206, 166, 127 and 66” are the ratio of the obtained Si/Al ratios of each catalyst).

4.1.2 Crystal structure (XRD)

Titanium silicalite-1, like the aluminosilicate ZSM-5, is a zeolite with an MFI structure. The X-ray diffraction results are given in Figure 4.1. The crystal structure of the samples can be identified as typical MFI structure based on the intensity of the five strong reflection peaks, 2θ as 8, 8.8, 14.8, 23.8, and 24.36 (Chengtian, 2002).

From the obtained XRD spectra, it can be concluded that the incorporation of aluminium into TS-1 catalyst does not affect significantly the MFI structure.

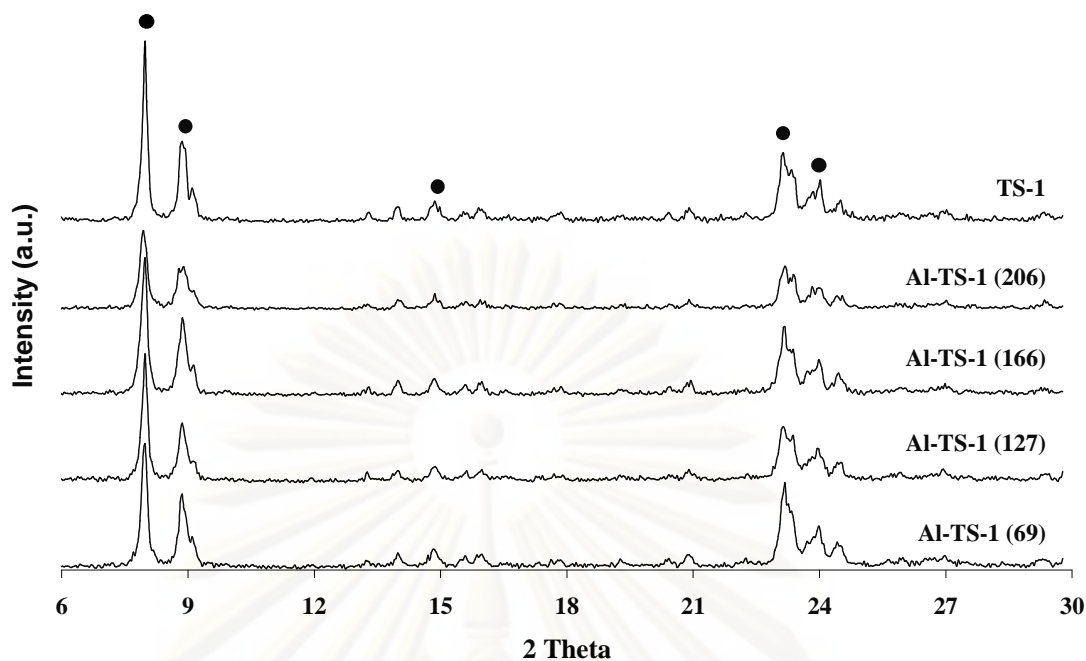


Figure 4.1 XRD patterns of TS-1 and Al-TS-1.

Since all the synthesized catalysts have the same crystal structure, any difference in the catalytic behavior, if exists, should not be the result of the crystal structure.

4.1.3 Fourier Transform Infrared (FT-IR)

FT-IR can be used to prove that Ti^{4+} has entered the silica lattice. The incorporation of titanium cation will form a tetrahedral group $\text{Ti}(\text{SiO})_4$ which will produce an absorption band around 960 cm^{-1} (Pirutko *et al.*, 2001).

The IR absorption spectra of all samples in $\text{Ti}(\text{SiO})_4$ absorption region are showed in Figure 4.2. Each sample shows the IR absorption band at 960 cm^{-1} which confirms that each sample has titanium cation exists in the $\text{Ti}(\text{SiO})_4$ structure (Chengtian, 2002).

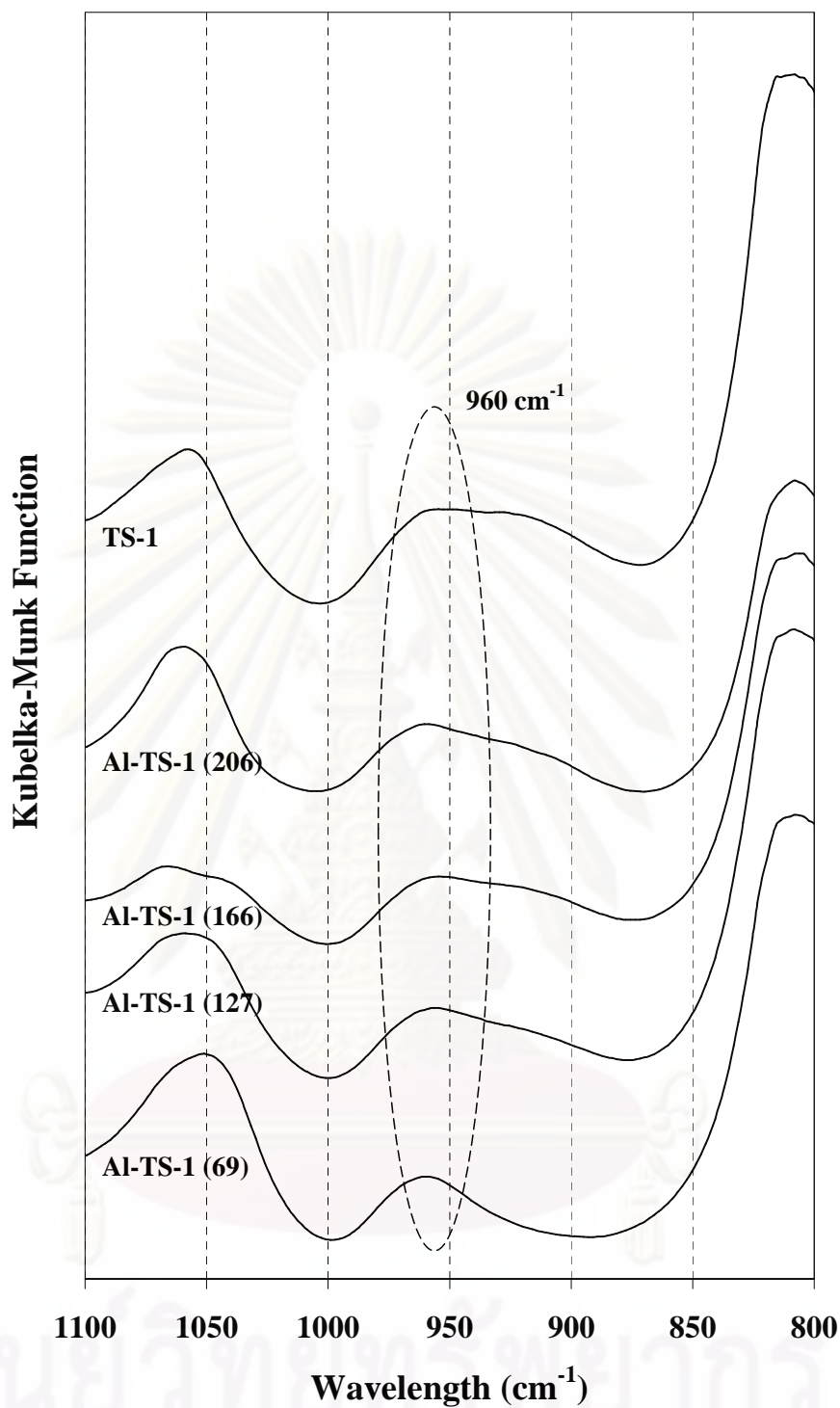


Figure 4.2 FT-IR spectra of TS-1 and Al-TS-1 catalysts.

Since catalyst characteristic determined from FT-IR measurement are not so different, the difference in the catalytic activity of each catalyst should not be the result of the difference in the titanium cation in the framework of the catalyst.

4.1.4 Surface Area (BET)

The surface area of TS-1 and all Al-TS-1 samples are tabulated in Table 4.2. All samples have surface area in the range 350 - 370 m²/g which is not so different. Hence, any difference observed during catalytic testing should not be the result of the difference in catalyst surface area.

Table 4.2 The surface area of TS-1 and Al-TS-1.

Catalysts	BET surface area (m ² /g)
TS-1	367
Al-TS-1 (206)	360
Al-TS-1 (166)	357
Al-TS-1 (127)	350
Al-TS-1 (69)	356

4.1.5 Temperature Programmed Desorption of ammonia (NH₃-TPD)

As demonstrated in sections 4.1.1 that the major difference of each catalyst is the amount of aluminium cation. Therefore, it is a topic of interest in this research to determine, if possible, why difference amount of aluminium causes difference catalytic behavior.

It is generally known that aluminium cation incorporated in the silicalite framework will act as an acid site. The acidic strength of aluminium cation inversely proportion to the amount of aluminium content while the density of acidic site proportion to the amount of aluminium content. It is hypothesized that the acidic property of the catalysts may relate to the catalytic behavior of the catalyst. Therefore, all catalysts are subjected to NH₃-TPD measurement. The measurement results are graphically showed in Figures 4.3 - 4.7. The peak deconvolution and fitting processes are carried out using a freeware "fityk" program.

The results suggest that the acidic site can be categorized into 3 groups, according to their desorption peaks. The first one locates around 160 - 200 °C which will be named here “the weak acid site”. The second one locates around 200 - 300 °C which will be named here “the medium strength acid site” and the last group locates higher than 300 °C and will be named here “the strong acid site”. The location of each peak and amount of peak type of the acidic site are summarized in Table 4.3.

Table 4.3 The strength and amount of the acid site of the catalysts.

Catalysts	Weak acid strength		Medium acid strength		Strong acid strength		Total acid site ($\mu\text{mol/g}$)
	Temp ($^{\circ}\text{C}$)	Site ($\mu\text{mol/g}$)	Temp ($^{\circ}\text{C}$)	Site ($\mu\text{mol/g}$)	Temp ($^{\circ}\text{C}$)	Site ($\mu\text{mol/g}$)	
	TS-1	163	63	238	14	-	
Al-TS-1 (206)	168	40	231	99	330	17	156
Al-TS-1 (166)	186	142	275	8	384	98	247
Al-TS-1 (127)	176	185	265	9	367	151	345
Al-TS-1 (69)	186	233	281	16	391	218	466

An important thing has to be mentioned here before interpreting the NH_3 -TPD results is each sample is subjected to heating at 550 °C before allowing to adsorb NH_3 . The sample treatment at such higher temperature results in removing hydroxyl (-OH) group from the sample surface inevitably. When the hydroxyl groups (Bronsted acid site) are removed, the Lewis acid site (the cations of Ti and Al) appear instead. Therefore, the NH_3 -TPD results may be used to quantitatively determine the amount of cations of Ti and Al exist on the catalyst surface by translating the amount of acidic site into the amount of Ti and Co ions on the surface. One should not be confused with the XRF results. The XRF results represent all Ti and Al ions, both accessible and inaccessible, to the reactants. While the NH_3 -TPD results represent only Ti and Al ions accessible to the reactants.

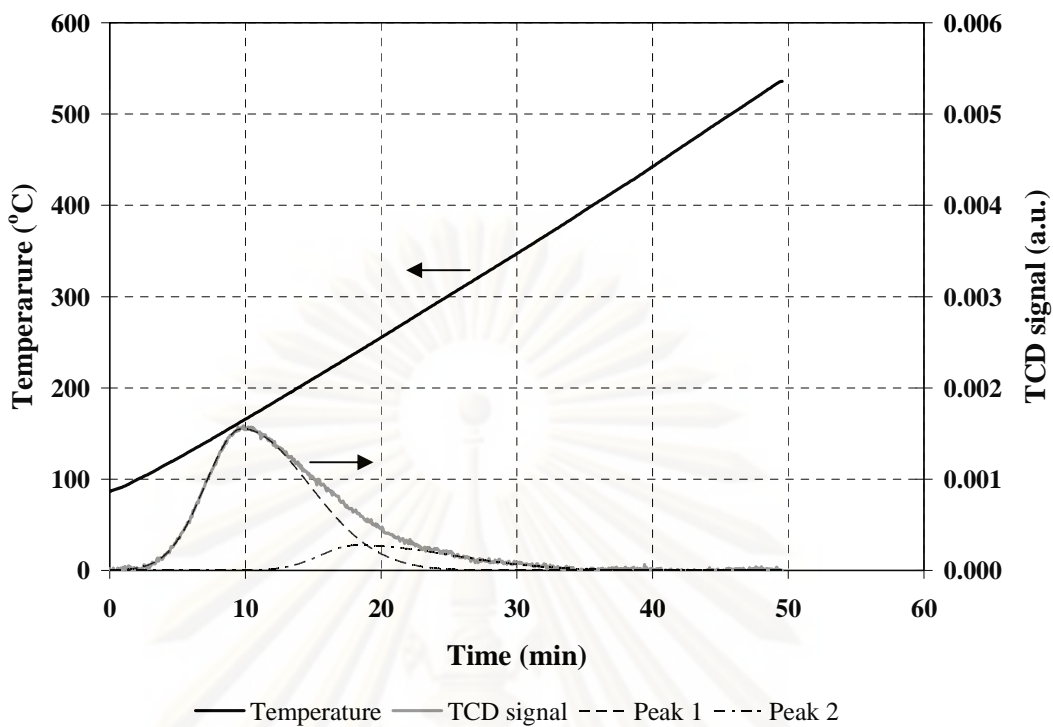


Figure 4.3 NH_3 -TPD of TS-1 catalyst.

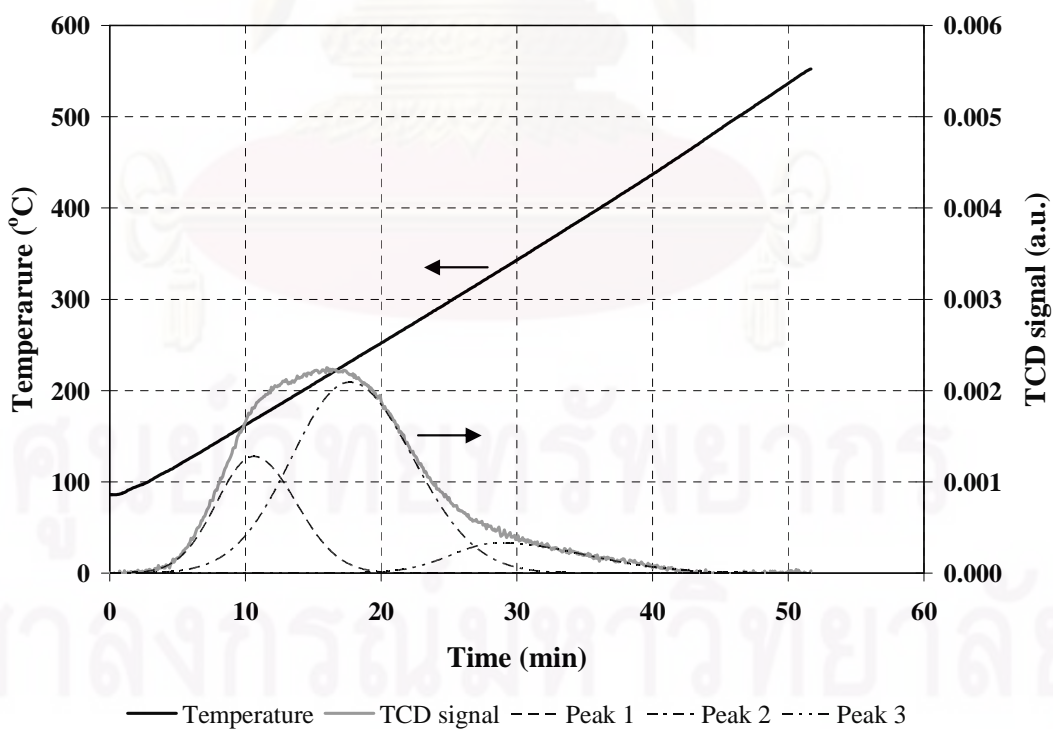


Figure 4.4 NH_3 -TPD of Al-TS-1 (206) catalyst.

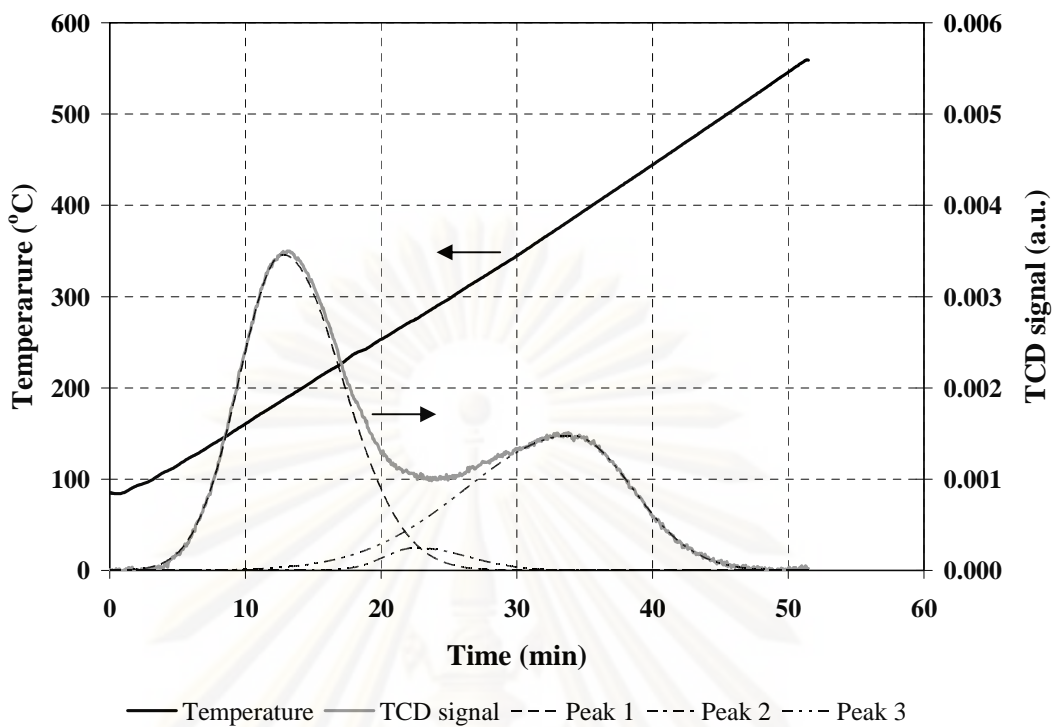


Figure 4.5 NH_3 -TPD of Al-TS-1 (166) catalyst.

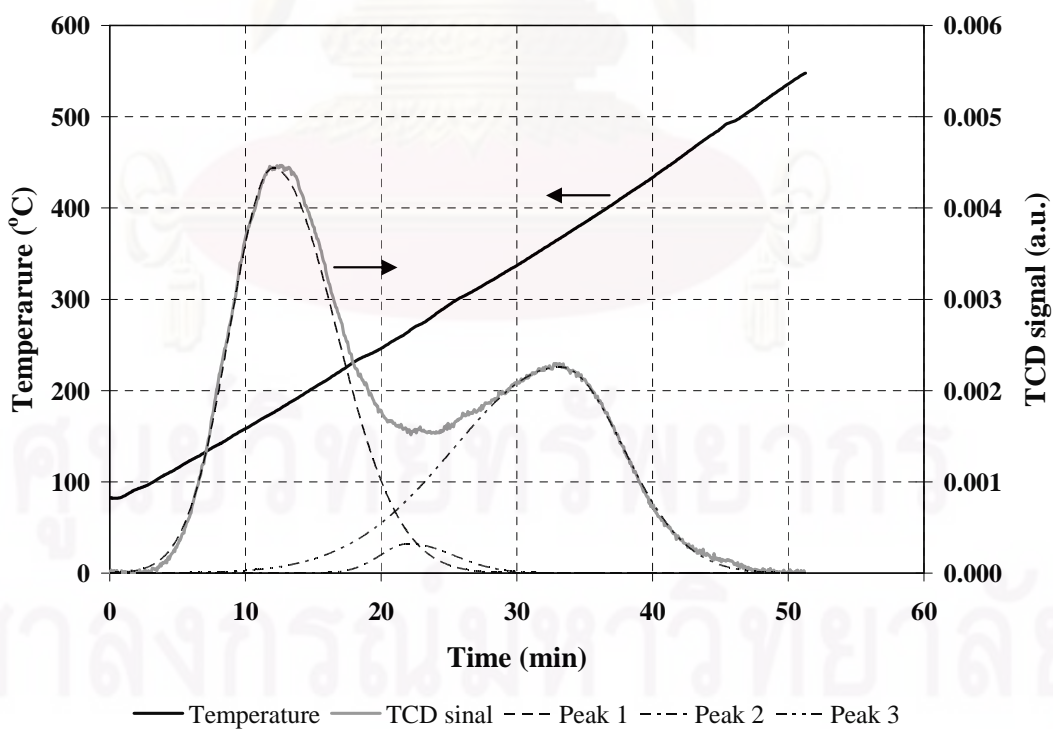


Figure 4.6 NH_3 -TPD of Al-TS-1 (127) catalyst.

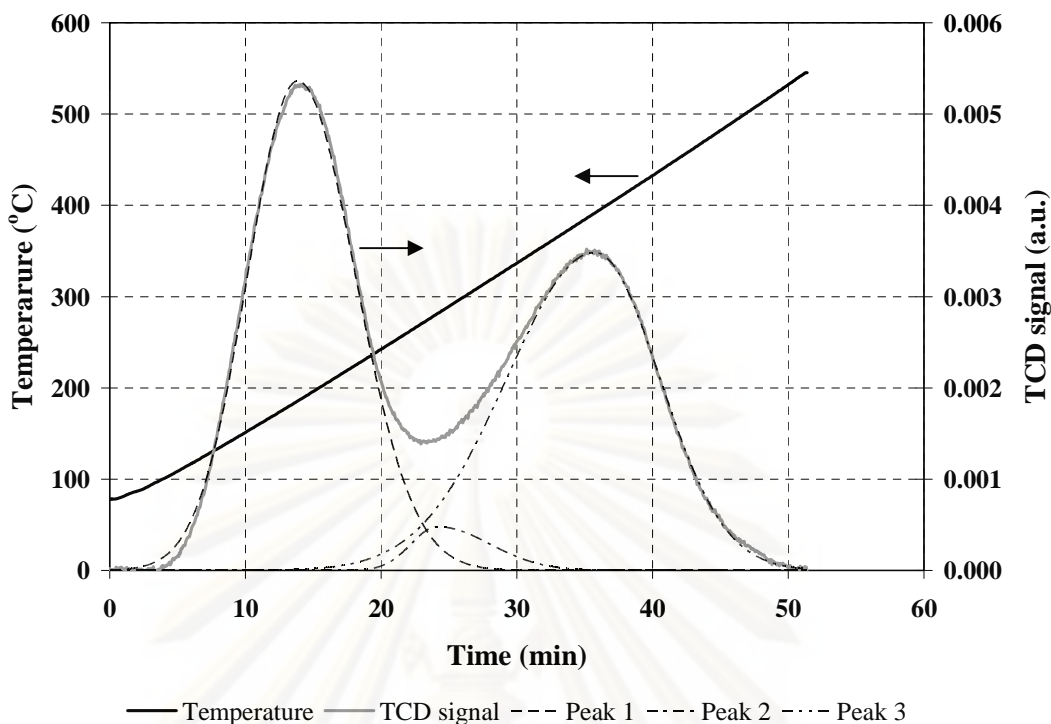


Figure 4.7 NH_3 -TPD of Al-TS-1 (69) catalyst.

The total area under the peaks represents the number of the acidic site on the catalyst surface. The larger the peak area, the higher the number of the acidic site. The position of each peak represents the strength of the acidic site. The higher the temperature of the desorption peak, the stronger the strength of the acidic site. TS-1 possesses the lowest number and the lowest strength of the acidic site. The amount and the strength of the acidic sites increase with the amount of Al^{3+} incorporated into the catalyst. Since NH_3 can interact only with Al^{3+} ions exist on the catalyst surface, the total area of the desorption peaks can be used to represent the number of Al^{3+} ions exist on the catalyst surface.

4.2 The catalytic reaction

The catalytic performance of TS-1 and Al-TS-1 catalysts are tested with the oxidation of toluene with H_2O_2 as oxidant. Reaction temperature and molar ratio of H_2O_2 : toluene used in this study are summarized in Table 4.4.

4.2.1 The effect of reaction temperature

It is found experimentally that the reaction between toluene and H_2O_2 over Al-TS-1 produces three reaction products : benzaldehyde, ortho-cresol and para-cresol. The distribution of each product depends on the reaction temperature and catalyst used.

Figure 4.8 illustrates the increase in the H_2O_2 conversion when the reaction temperature is increased. This phenomenon is due to the following reasons.

1. The reaction rate increase with the increasing reaction temperature.
2. The solubility of toluene in water increases with the increasing reaction temperature. Thus, providing more reactant for the reaction.

Table 4.4 Reaction conditions for TS-1 and Al-TS-1.

Catalysts	Reaction temperature (°C)	Molar ratio of H ₂ O ₂ : toluene
TS-1	70	1:1
	110	1:1
	110	2:1
	120	1:1
	120	2:1
Al-TS-1 (206)	70	1:1
	110	1:1
	110	2:1
	120	1:1
	120	2:1
Al-TS-1 (166)	70	1:1
	110	1:1
	110	2:1
	120	1:1
	120	2:1
Al-TS-1 (127)	70	1:1
	110	1:1
	110	2:1
	120	1:1
	120	2:1
Al-TS-1 (69)	70	1:1
	110	1:1
	110	2:1
	120	1:1
	120	2:1

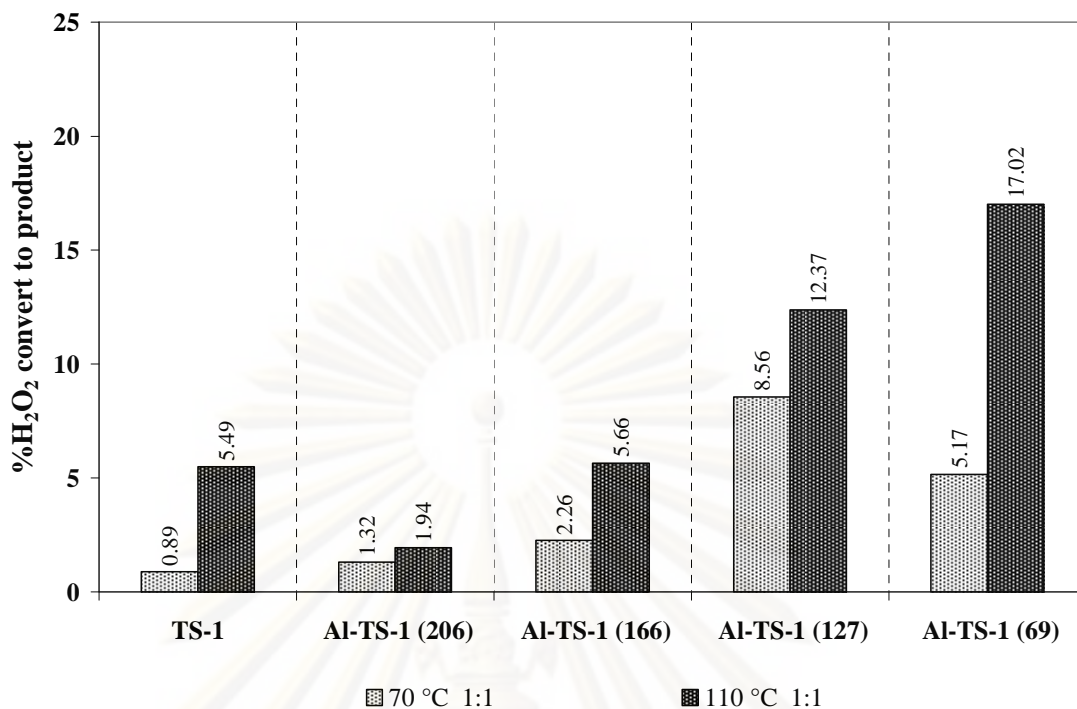


Figure 4.8 %H₂O₂ convert to product of molar ratio H₂O₂ : toluene = 1:1.

Figure 4.9 exhibits the productivity of each product when the molar ratio H₂O₂ : toluene = 1:1. The experimental results showed below reveal that the productivity of benzaldehyde increases with the increasing reaction temperature. On the contrary, the productivity of o-cresol and p-cresol is hardly change except TS-1 and Al-TS-1 (69).

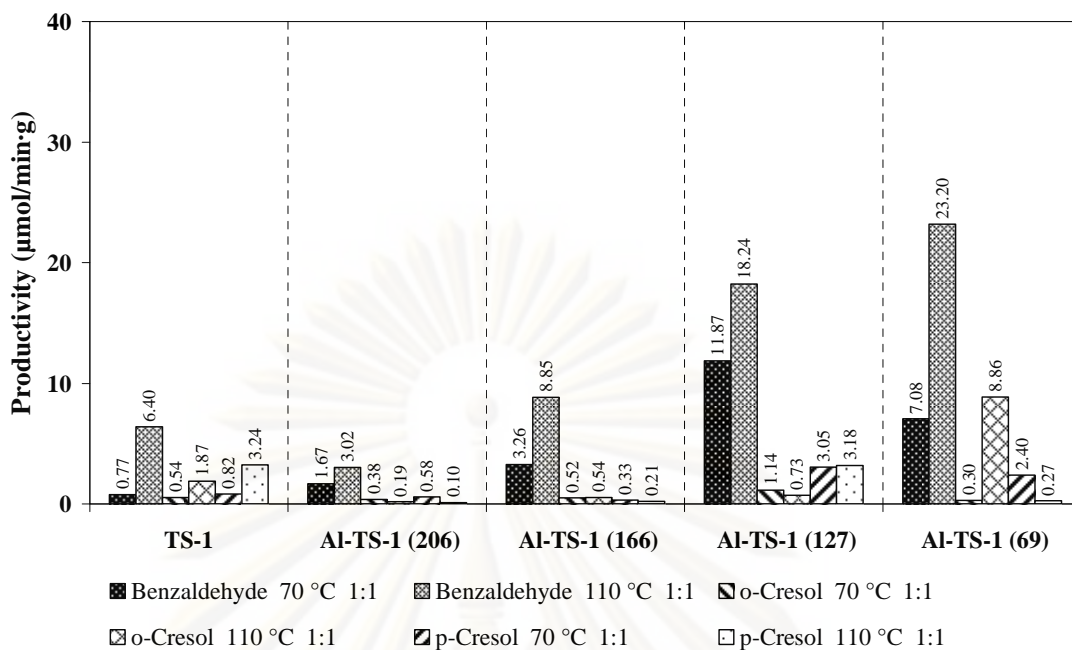


Figure 4.9 Productivity of molar ratio H_2O_2 : toluene = 1:1.

Figure 4.10 illustrates the %selectivity of molar ratio H_2O_2 : toluene = 1:1. It is found that adding amount of aluminium increases the selectivity towards benzaldehyde. On the other hand, the selectivity of cresols decreases except Al-TS-1 (69).

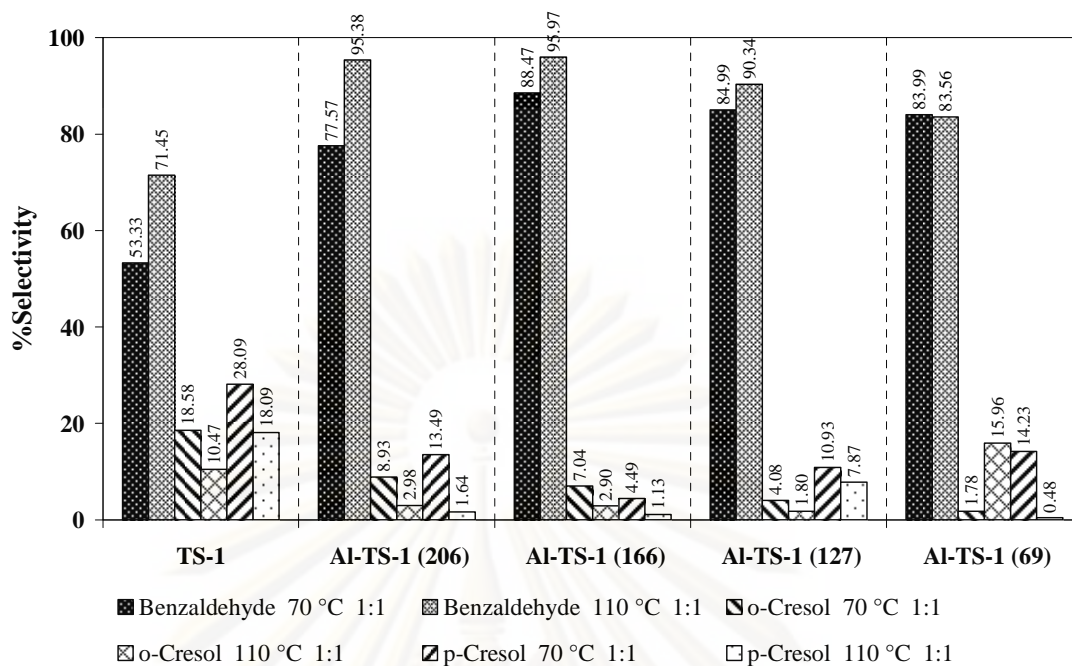


Figure 4.10 %Selectivity of molar ratio H_2O_2 : toluene = 1:1.

The results obtained from the different reaction temperature (110 and 120 °C), exhibited in Figures 4.11 - 4.16, also similar to those exhibited in Figures 4.8 - 4.10. The only difference is Al-TS-1 (69) catalyst in Figures 4.11 - 4.13 and Al-TS-1 (166) catalyst in Figures 4.14 - 4.16. The H_2O_2 converts to product and productivity toward benzaldehyde decreased. It should be noted here that the increase in the solubility of toluene can result in different results. If, initially the concentration of toluene is too low, the increase in the solubility of toluene will provide more toluene on the catalyst surface. This will result in the increase of conversion. Because the catalyst surface is hydrophobic by nature, the adsorption of toluene on the catalyst surface is much better than the adsorption of H_2O_2 . If too high toluene exists on the catalyst surface, the reaction rate will decrease.

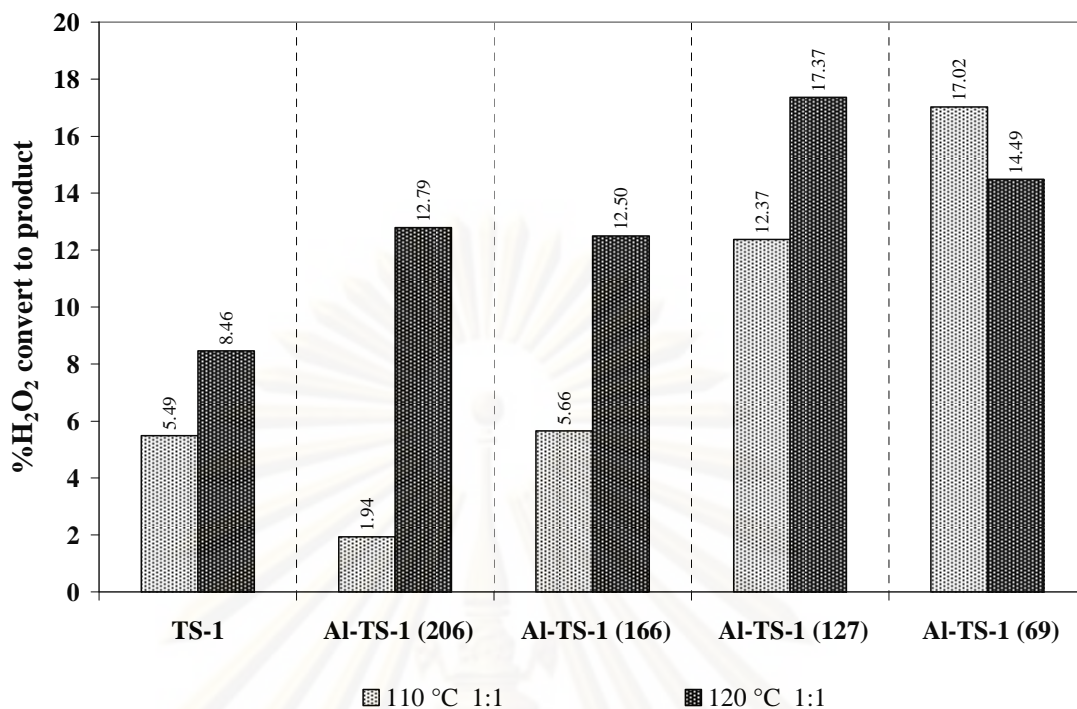


Figure 4.11 %H₂O₂ convert to product of molar ratio H₂O₂ : toluene = 1:1.

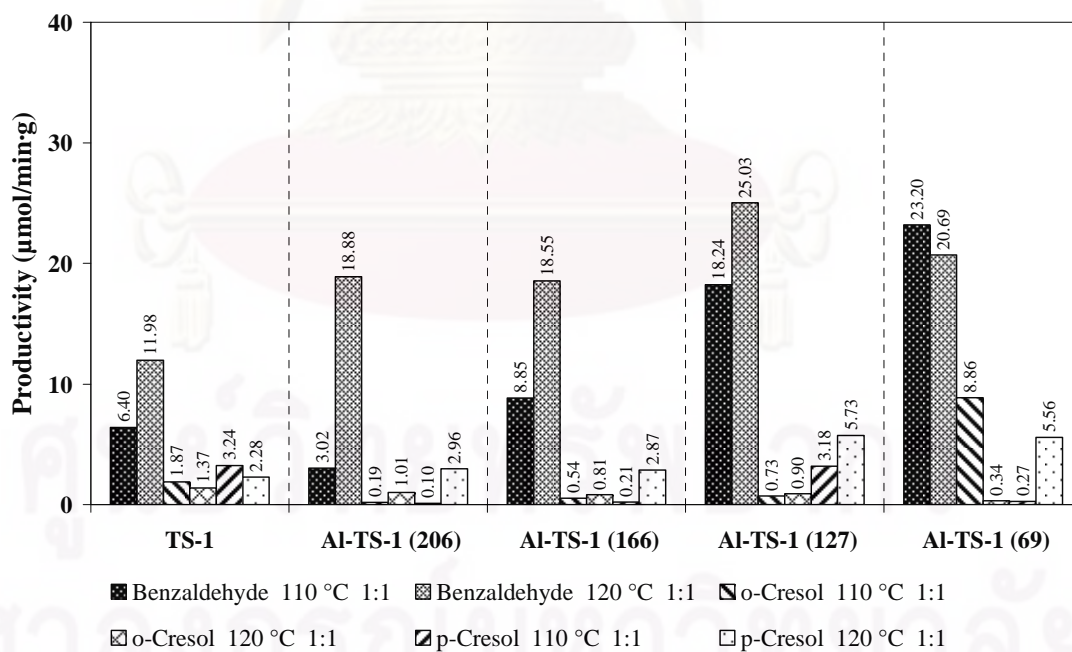


Figure 4.12 Productivity of molar ratio H₂O₂ : toluene = 1:1.

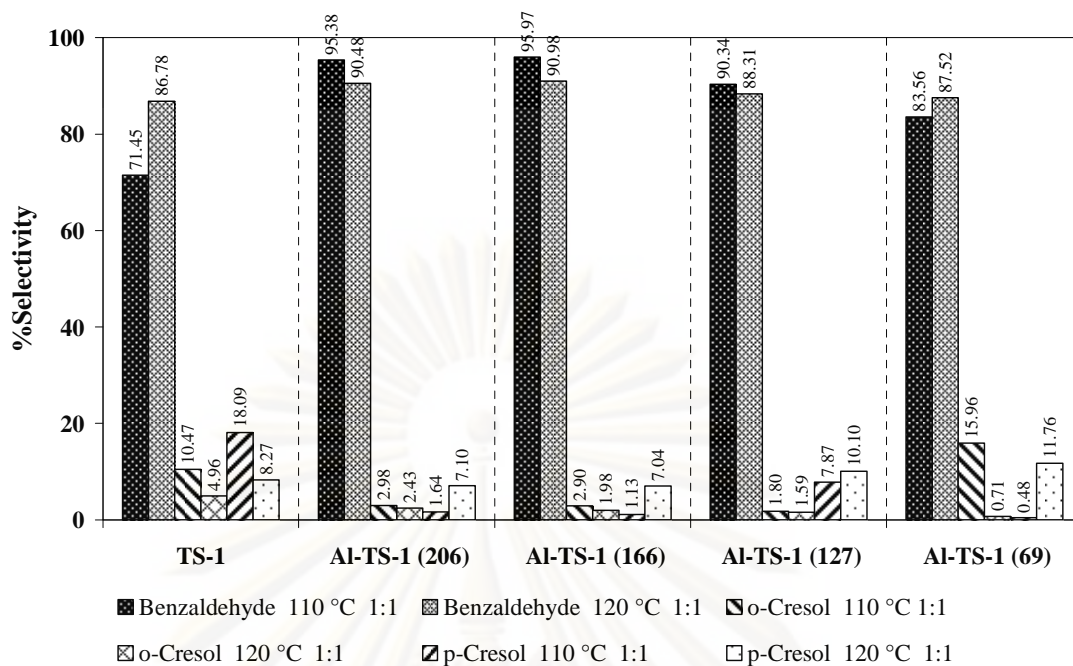


Figure 4.13 %Selectivity of molar ratio H_2O_2 : toluene = 1:1.

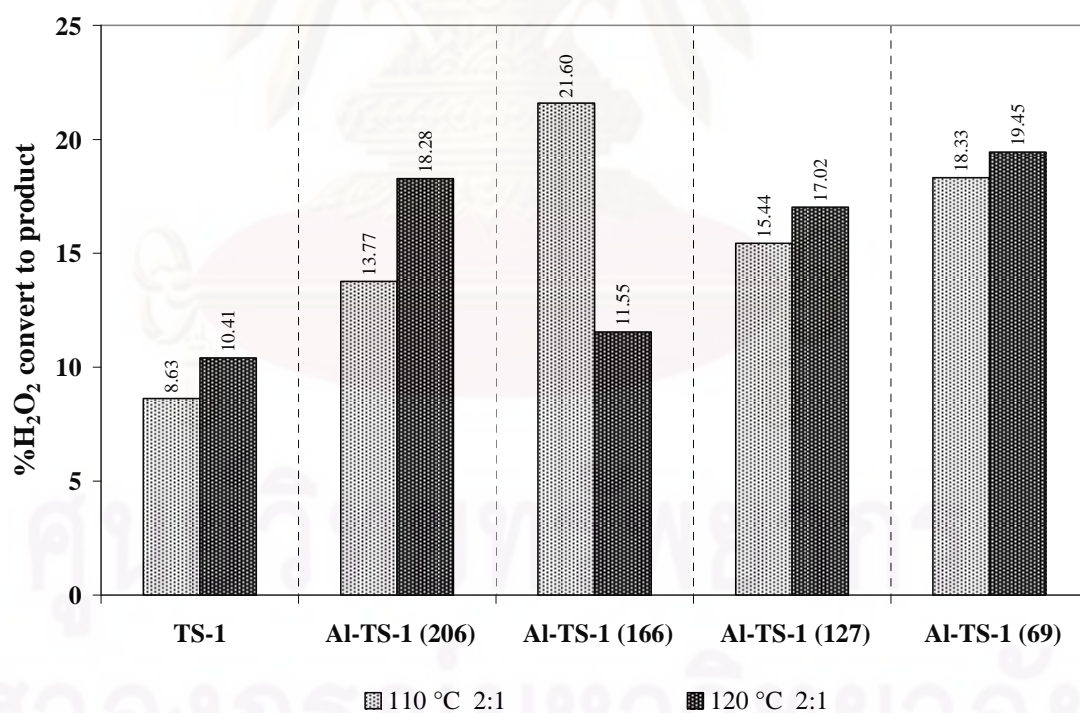


Figure 4.14 % H_2O_2 convert to product of molar ratio H_2O_2 : toluene = 2:1.

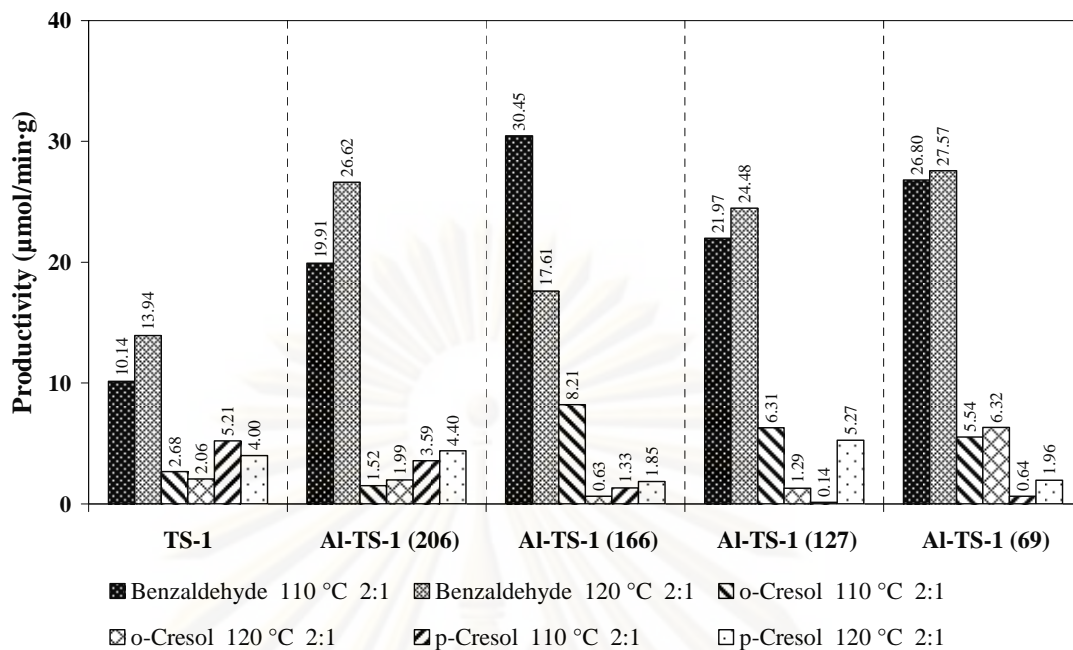


Figure 4.15 Productivity of molar ratio H_2O_2 : toluene = 2:1.

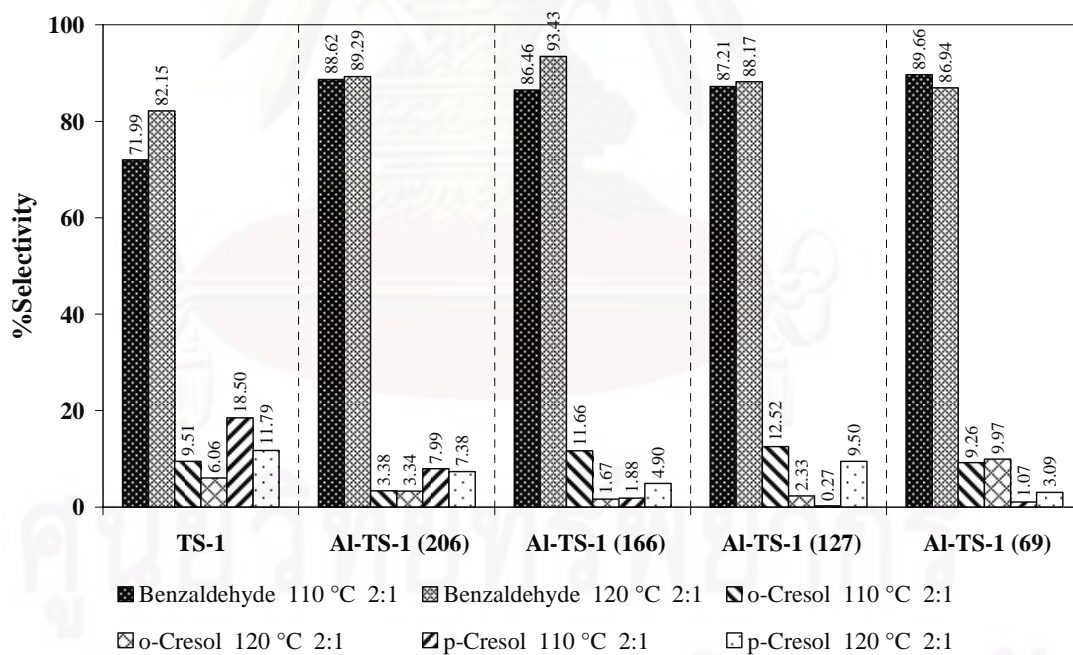


Figure 4.16 %Selectivity of molar ratio H_2O_2 : toluene = 2:1.

4.2.2 The effect to molar ratio of reactant (H_2O_2 : Toluene)

Another parameter affecting the reaction to be discussed is the molar ratio between H_2O_2 and toluene. The effect of molar ratio of reactants (H_2O_2 : toluene) on the conversion of H_2O_2 obtained at the reaction temperature $110\text{ }^\circ\text{C}$ is illustrated in Figures 4.17 - 4.19. Figure 4.17 shows % H_2O_2 , Figure 4.18 shows productivity and Figure 4.19 shows product selectivity. It is observed that increasing the ratio H_2O_2 : toluene from 1:1 to 2:1 results in increasing H_2O_2 convert to product and productivity toward benzaldehyde. But the %selectivity of benzaldehyde has both increase and decrease. %Selectivity of benzaldehyde decreases in case of Al-TS-1 (206), Al-TS-1 (166) and Al-TS-1 (127) due to increasing productivity toward o-cresol and p-cresol prefer than the productive toward benzaldehyde.

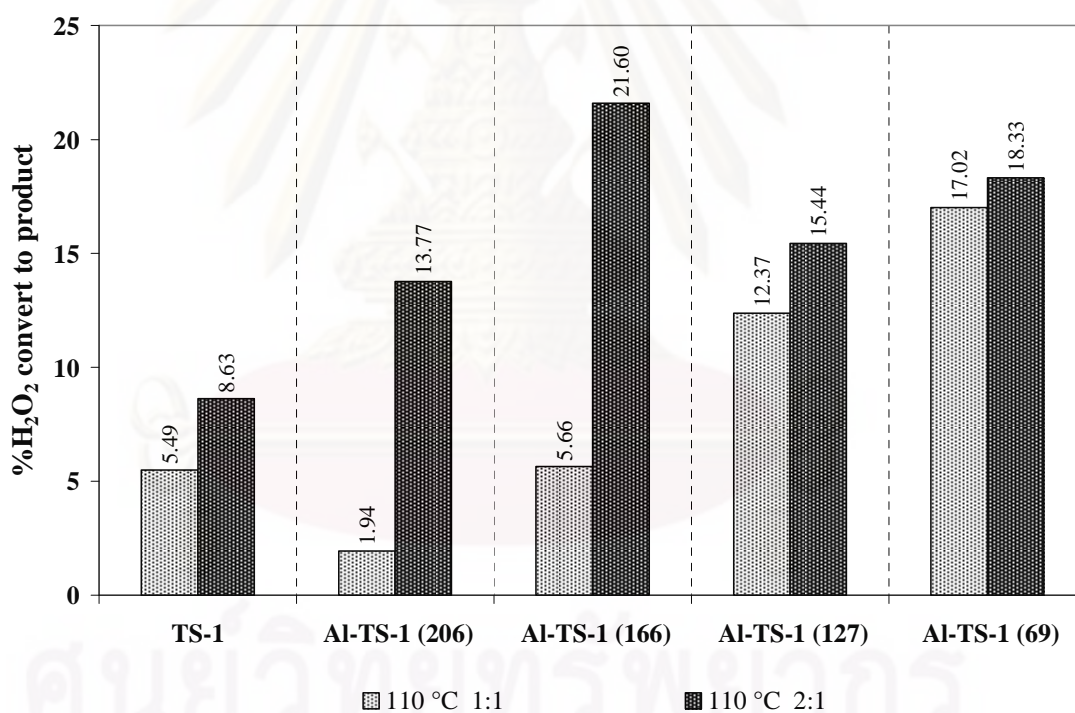


Figure 4.17 % H_2O_2 convert to product at $110\text{ }^\circ\text{C}$.

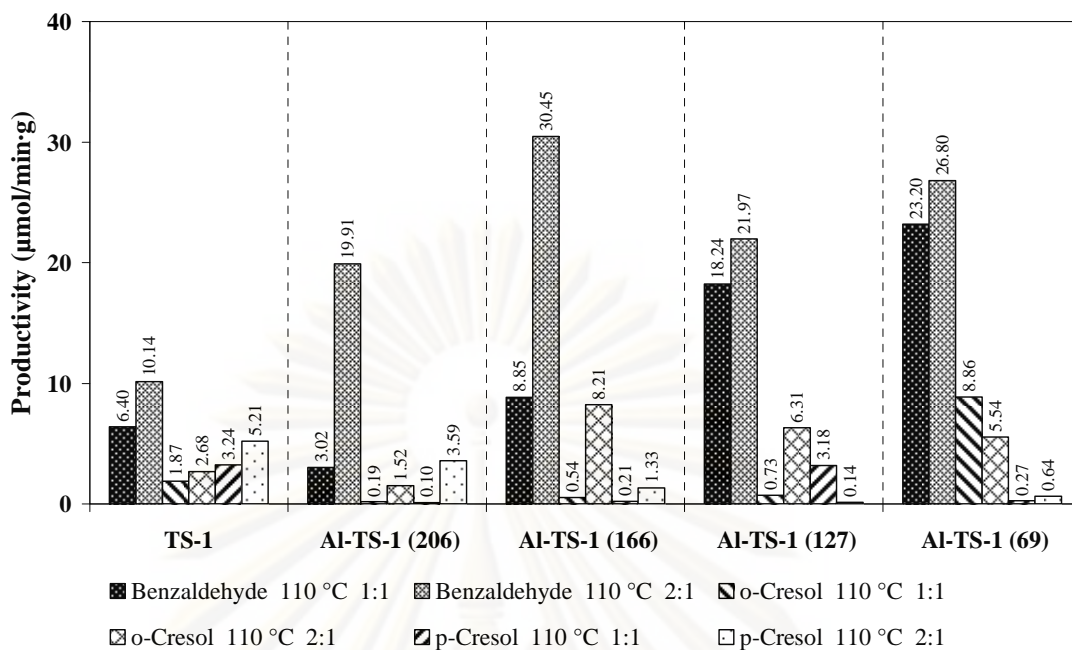


Figure 4.18 Productivity at 110 °C.

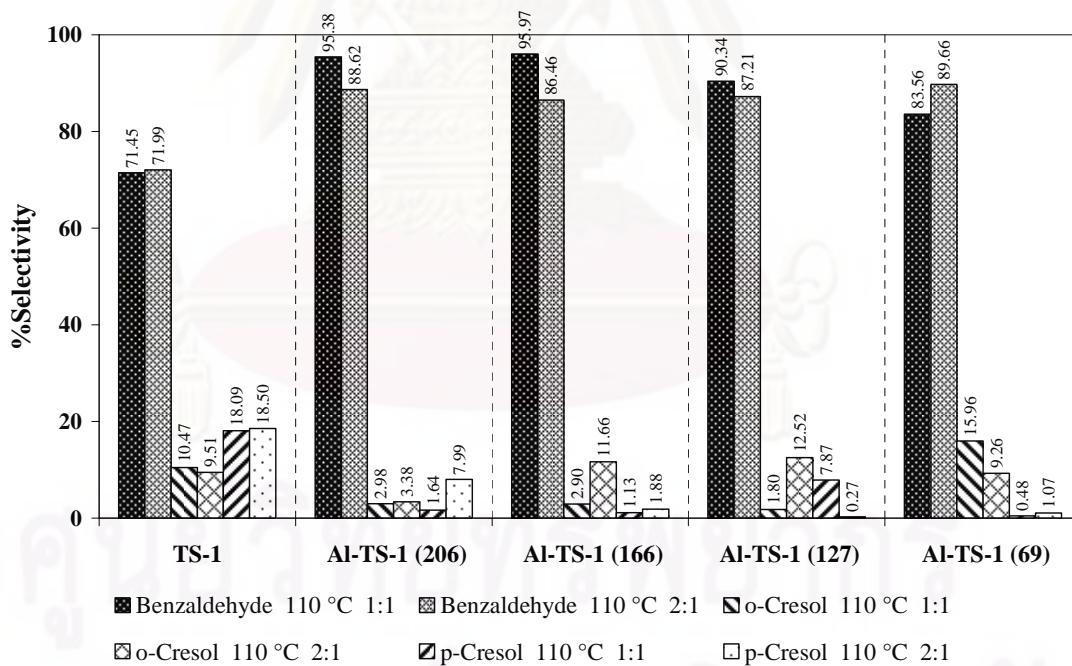


Figure 4.19 %Selectivity at 110 °C.

Figures 4.20 – 4.22 show the H_2O_2 conversion, productivity and selectivity at reaction temperature $120\text{ }^\circ\text{C}$ respectively. The results also similar to those exhibited in Figures 4.17 - 4.19. The difference is Al-TS-1 (166) and Al-TS-1 (127) catalysts in Figures 4.20 - 4.22. The H_2O_2 converts to product and productivity toward benzaldehyde are slightly decreased. As discussed earlier, the maximum reaction rate will occur when H_2O_2 and toluene both exist on the catalyst surface in an appropriate ratio. If one reactant occupies too high surface area, the reaction rate will be lower. The experimental results show that for TS-1, Al-TS-1 (206), and Al-TS-1 (69) their surfaces are likely occupied by too much toluene. When the amount of H_2O_2 injected is increased twice, more H_2O_2 can adsorb on the catalyst which results in the increase in H_2O_2 conversion. For Al-TS-1 (166) and Al-TS-1 (127), however, using the ratio H_2O_2 : toluene equals to 1:1 may already provide the appropriate ratio of H_2O_2 per toluene on the catalyst surface. Using H_2O_2 : toluene equals to 2:1 results in too much H_2O_2 on the catalyst surface which results in a slight decrease in H_2O_2 conversion.

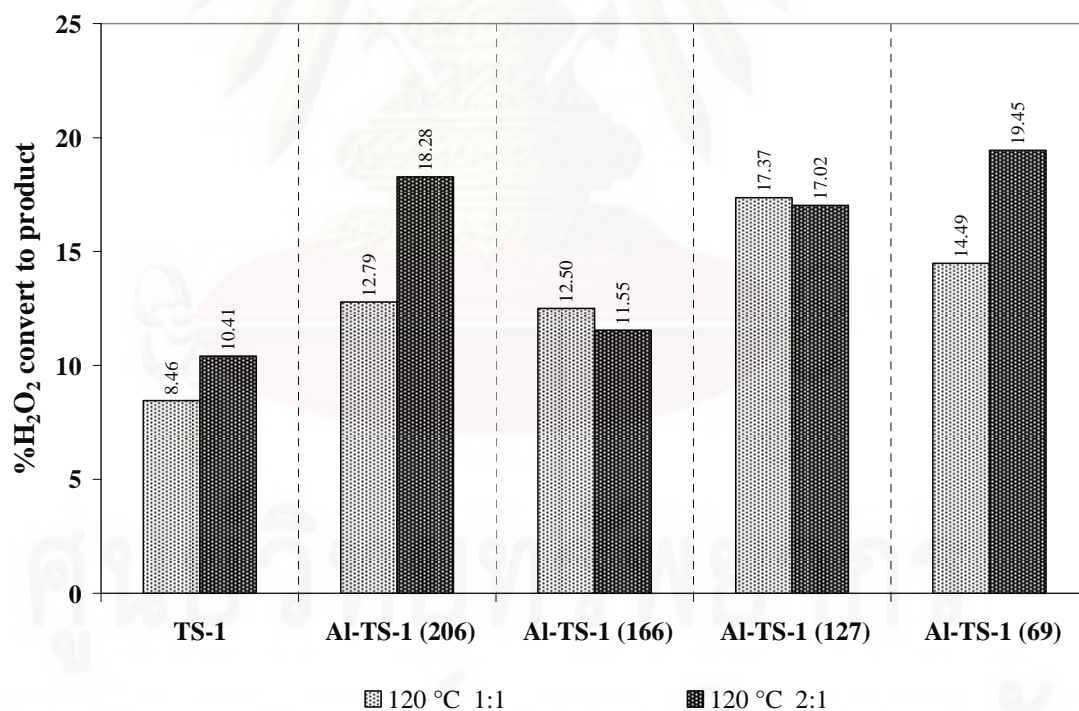


Figure 4.20 % H_2O_2 convert to product at $120\text{ }^\circ\text{C}$.

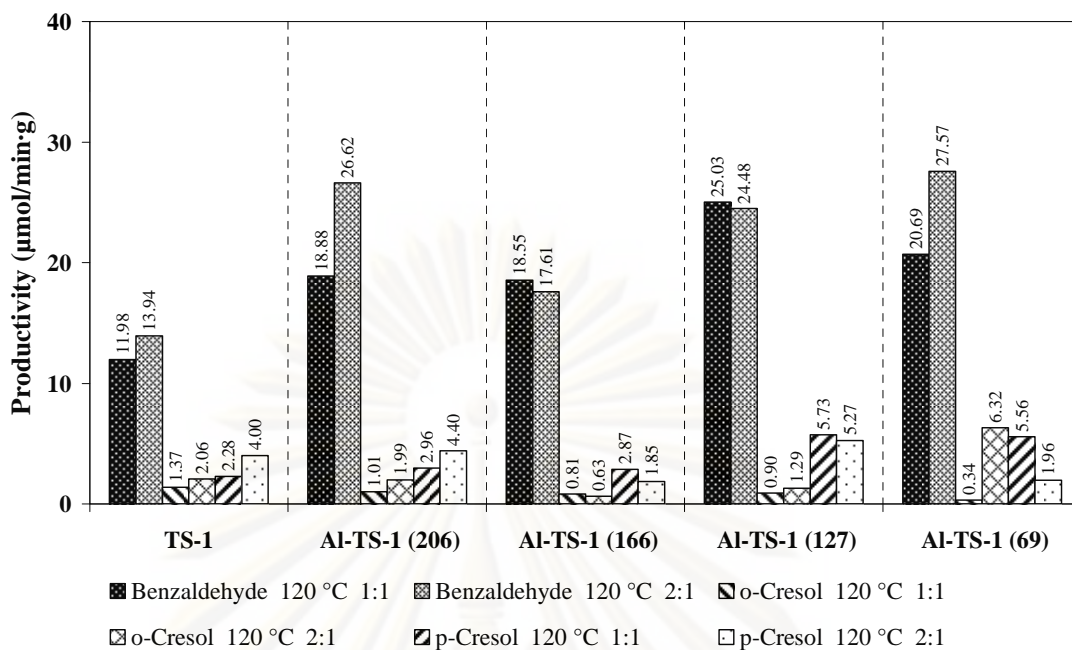


Figure 4.21 Productivity at 120 °C.

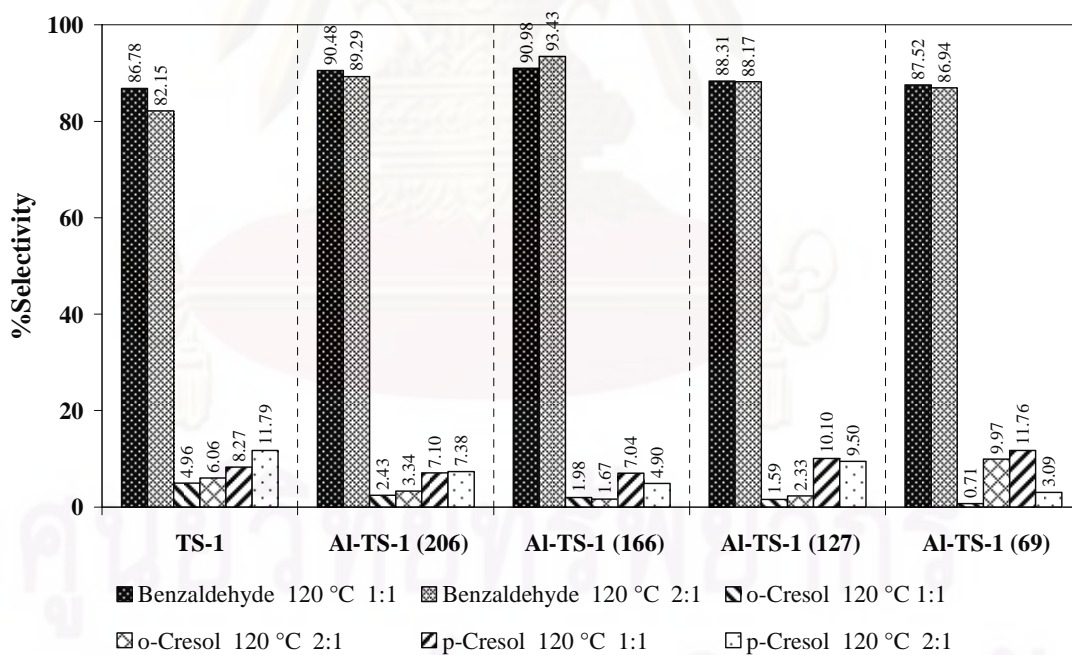


Figure 4.22 %Selectivity at 120 °C.

4.3 Proposed mechanism for the formation of benzaldehyde and cresols

It has been demonstrated above that the reaction between toluene and H_2O_2 over TS-1 and Al-TS-1 results in benzaldehyde (oxidation at the side chain methyl group) and cresols (electrophilic substitution of H atom of the aromatic ring). Both reactions are summarized in Figure 4.17.

In this section, the mechanisms for the formation of benzaldehyde and cresols will be proposed.

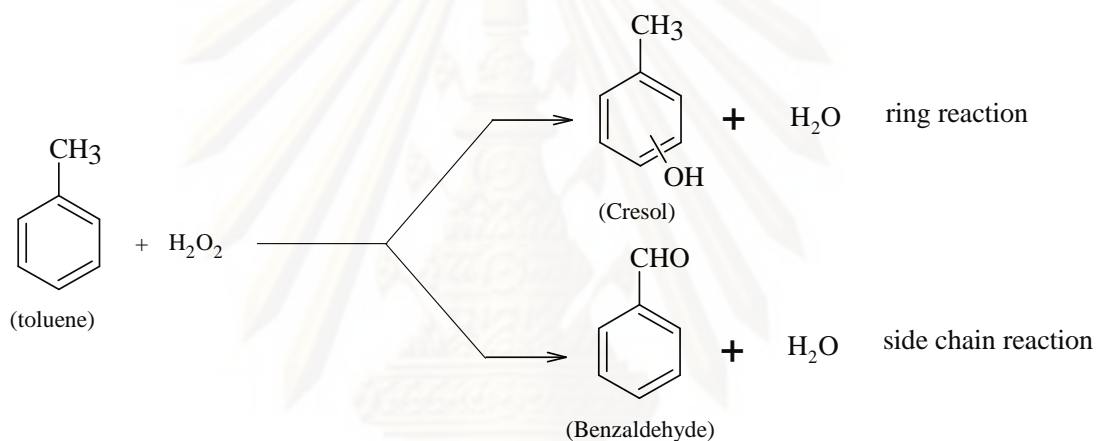


Figure 4.23 The oxidation of toluene at the side chain and benzene ring.

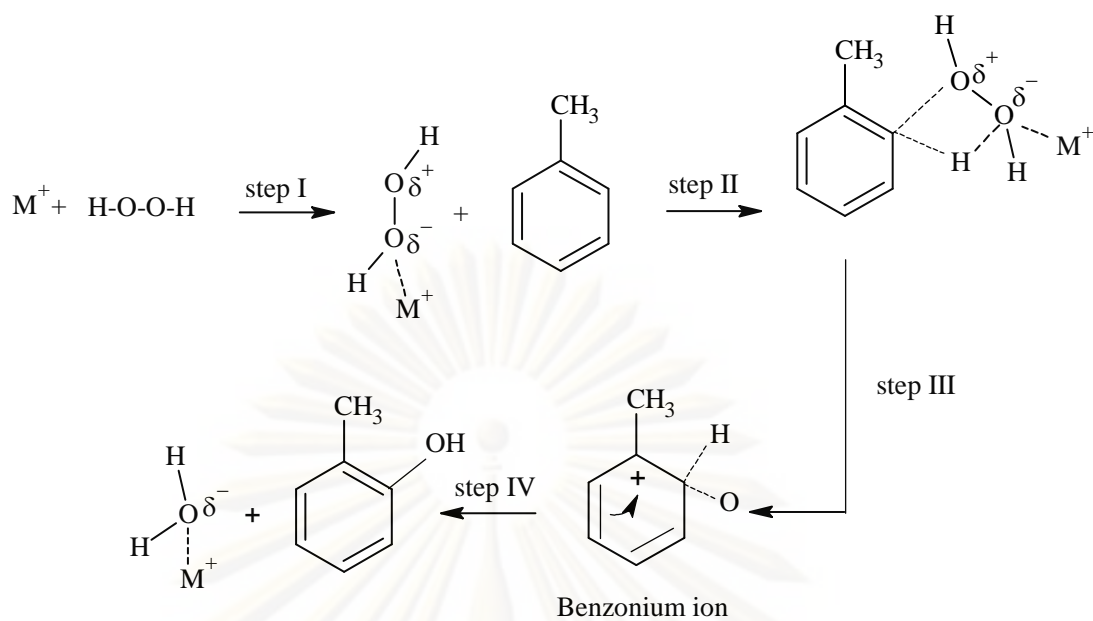
4.3.1 Proposed mechanism for the formation of cresols

It is generally known that the substitution position of the second group on the aromatic ring depends on the ability of the first substitution group to withdraw or supply electron to the ring. In case the first substitution group is an alkyl group ($-\text{CH}_3$ in case of toluene), the second substitution will prefer the ortho- or para- position. In our case, therefore, the appearance of o-cresol and p-cresol with the absence of m-cresol is not beyond expectation.

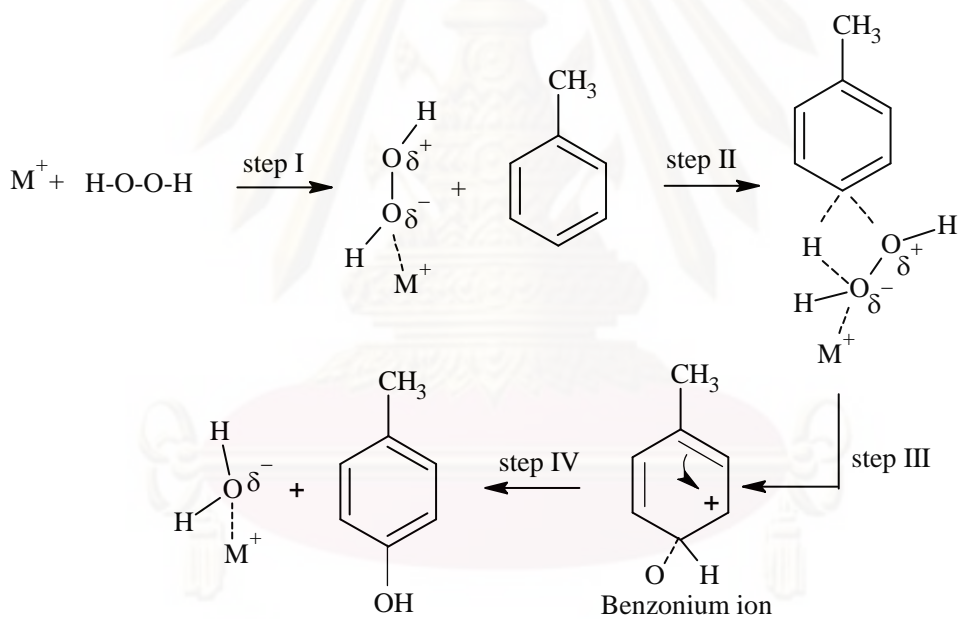
The mechanisms for the formation of o-cresol and p-cresol are showed in Figure 4.18. The mechanism of cresol is proposed to consist of the following four steps:

1. The metal active sites (Ti^{4+} or Al^{3+}) convert H_2O_2 to a strong electrophile by forming a complex and polarizing the (OH)-(OH) bond.
2. The electrophile (-OH) attacks to one carbon atom of benzene ring at ortho- or para- position, using two pi electrons from the pi cloud to form a sigma bond with ring carbon atom. This carbon atom becomes sp^3 -hybridized. The benzene ring acts as a pi electron donor, or nucleophile, toward the electrophilic reagent.
3. The benzenium ion, in which the positive charge is delocalized by resonance to the carbon atom at ortho and para to the carbon to which the OH radical became attached; that is ortho and para to the sp^3 carbon atom.
4. The substitution is completed by loss of a proton from sp^3 carbon atom, the same atom to which the electrophilic became attached.

The reaction proceeds via this mechanism should produce only cresol.



(a)



(b)

M^+ is Ti^{4+} and second metal

Figure 4.24 The mechanism of cresol in the oxidation of toluene (a) o-cresol and (b)

p-cresol

4.3.2 Proposed mechanism for the formation of benzaldehyde

The reaction scheme of benzaldehyde formation is expected to be different from the mechanism of cresol formation. The hydrogen atoms of the alkyl group attached to the ring can be replaced by free radicals (such as $\text{H-O}\cdot$ and $\text{H-O-O}\cdot$) more easily than hydrogen atom of the ring. Such free radicals may be generated from the decomposition of H_2O_2 by the presence of some cations. It is hypothesized that the formation of benzaldehyde will follow the mechanism similar to the halogenation of saturated hydrocarbon. It is known that the presence of several transition metal cations, strong Lewis acid, promote the decomposition of H_2O_2 . In our reaction, Al^{3+} which can act as a strong Lewis acid site which promotes the decomposition of H_2O_2 . The free radicals generated during the decomposition of H_2O_2 can combine with each other to form H_2O and O_2 or react with toluene to form benzaldehyde and/or cresols. In our system, since the surface of the catalyst is hydrophobic in nature, a significant amount of toluene exists on the catalyst surface. The chance for the free radicals generated during the catalytic decomposition of H_2O_2 to react with toluene is, therefore, high. When the temperature of the aqueous phase is further increased, the solubility of toluene in water increases rapidly which results in a much larger amount of toluene on the catalyst surface. The chance for the free radicals generated during the catalytic decomposition of H_2O_2 to react with toluene is, therefore, increased rapidly. This is the explanation why the formation of benzaldehyde increases abruptly when the temperature of the aqueous solution is increased from 70 to 110 °C.

Too much temperature increasing may produce a negative effect due to too much toluene on the catalyst surface will prevent H_2O_2 from being catalytically decomposed by H_2O_2 . This may be the explanation why when the temperature of the aqueous solution is further increased from 110 °C to 120 °C, the conversion of H_2O_2 increases only slightly or in some case, Al-TS-1 (69) at molar ratio H_2O_2 : toluene = 1:1 and Al-TS-1 (166) at molar ratio H_2O_2 : toluene = 2:1, decreases.

The effect of too high amount of benzaldehyde on the catalyst surface can be attenuated by increasing the amount of H_2O_2 injected into the system. The increase amount of injected H_2O_2 provides more free radical for the oxidation of toluene to benzaldehyde which requires two H_2O_2 molecule per one benzaldehyde molecule formed. The difference of the effect of the increase amount of the injected H_2O_2 of each catalyst possibly due to each catalyst has different hydrophilic nature. At reaction temperature is $110\text{ }^\circ\text{C}$, the catalysts showing pronouncing effects, Al-TS-1 (206) and Al-TS-1 (166), should have more hydrophilic surface than the rest. But at reaction temperature $110\text{ }^\circ\text{C}$, Al-TS-1 (166) and Al-TS-1 (127) are slightly decrease because of too much toluene on the catalyst surface will prevent H_2O_2 from being catalytically decomposed by H_2O_2 .



CHAPTER V

CONCLUSION AND RECOMMENDATION

The present work investigates the oxidation of toluene by hydrogen peroxide at elevated temperature over TS-1 and Al-TS-1 catalysts having different Si/Al ratios. The conclusions and recommendations for future study which can be drawn from the experimental results are summarized in sections 5.1 and 5.2, respectively.

5.1 Conclusions

1. The reaction path way in the oxidation has two paths. The first is the ring oxidation and the other one is the side chain oxidation. Toluene oxidation gives cresol (ring oxidation) and benzaldehyde (side chain oxidation) products.

2. All TS-1 and Al-TS-1 catalysts synthesized by hydrothermal and aluminium are added by incorporation in the step of synthesis have the MFI structure and the presence of Ti^{4+} present in the framework which following the normal characteristic of TS-1.

3. Increasing molar ratio of H_2O_2 per toluene from 1:1 to 2:1 to increases benzaldehyde formation.

4. Increasing of reaction temperature increases the reaction rate. But the conversion of H_2O_2 increases only slightly or decreases in some case.

5.2 Recommendations for further study

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

1. In the experiments, the fresh catalysts are only used in the reaction. Further study on catalyst stability and regeneration is still needed.
2. The catalyst preparation recipes should be studied to find a proper procedure that can better control the catalyst composition.
3. Another method that can change the boiling point temperature of water is reducing the pressure above the water surface. It is interesting to operate the reactor under the reduced pressure to see whatever the solubility of toluene can be increased and can lead to the increase in the reaction rate or not.

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APPENDICES

ศูนย์วิทยทรัพยากร
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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,

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

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

$$\begin{aligned} \text{Mole of Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 \text{ required} &= 0.3273/50 \\ &= 6.546 \times 10^{-3} \text{ mole} \\ \text{amount of Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 &= (6.546 \times 10^{-3}) \times (340.36) \times (100/97) \\ &= 2.2970 \text{ g} \end{aligned}$$

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.

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

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

Si/Al atomic ratio = 150

$$\begin{aligned}\text{Mole of Al(NO}_3)_3 \cdot 9\text{H}_2\text{O required} &= 0.3273/150 \\ &= 2.18 \times 10^{-3} \text{ mole} \\ \text{amount of Al(NO}_3)_3 \cdot 9\text{H}_2\text{O} &= (2.18 \times 10^{-3}) \times (375.13) \\ &= 0.82 \text{ g}\end{aligned}$$

which used in A1 and A2 solutions.



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APPENDIX B

CALCULATION OF METAL QUANTITY

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

The XRF results were reported in the amount of metal oxide as shown in Table B1.

Table B1 Data of TS-1 from XRF technique and molecular weights.

Metal oxide	Concentration (% wt)	Molecular weight (MW)
Na ₂ O	0.141	61.9789
Al ₂ O ₃	0.093	101.9613
SiO ₂	96.648	60.0843
SO ₃	0.291	80.0632
TiO ₂	2.686	79.8658
MnO ₂	0.103	86.9368
Fe ₂ O ₃	0.037	159.6922

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

1. Mole of metal oxides

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

$$\text{Mole of Al}_2\text{O}_3 = \frac{0.093}{101.9613} = 0.000912 \text{ mole}$$

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

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

$$\begin{aligned} \text{Mole of Al} &= 2 \times 0.000912 \\ &= 0.001824 \text{ mole} \end{aligned}$$

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

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

$$\text{Mole\% of Al} = \frac{0.001824}{1.65019} = 0.001105 \text{ mole\%}$$

Table B2 Calculated composition of TS-1.

Compound	TS-1		mole of metal oxide	mole of cation	mole % of cation	Mol %
	% wt	MW				
Na ₂ O	0.141	61.9789	0.002275	0.004550	0.002757	0.275721
Al ₂ O ₃	0.093	101.9613	0.000912	0.001824	0.001105	0.110546
SiO ₂	96.648	60.0843	1.608540	1.608540	0.974758	97.47583
SO ₃	0.291	80.0632	0.003635	-	-	-
TiO ₂	2.686	79.8658	0.033631	0.033631	0.020380	2.038028
MnO ₂	0.103	86.9368	0.001185	0.001185	0.000718	0.071796
Fe ₂ O ₃	0.037	159.6922	0.000232	0.000463	0.000281	0.028081

Table B3 Calculated composition of Al-TS-1 (206).

Al-TS-1 (206)			mole of metal oxide	mole of cation	mole % of cation	Mol %
Compound	% wt	MW				
Na ₂ O	0.57	61.9789	0.009197	0.018393	0.011074	1.107422
Al ₂ O ₃	0.397	101.9613	0.003894	0.007787	0.004689	0.468854
SiO ₂	96.281	60.0843	1.602432	1.602432	0.964788	96.47876
SO ₃	0.171	80.0632	0.002136	-	-	-
TiO ₂	2.541	79.8658	0.031816	0.031816	0.019156	1.915561
Fe ₂ O ₃	0.039	159.6922	0.000244	0.000488	0.000294	0.029408

Table B4 Calculated composition of Al-TS-1 (166).

Al-TS-1 (166)			mole of metal oxide	mole of cation	mole % of cation	Mol %
Compound	% wt	MW				
Na ₂ O	0.102	61.9789	0.001646	0.003291	0.001992	0.19918
Al ₂ O ₃	0.494	101.9613	0.004845	0.009690	0.005864	0.586382
SiO ₂	96.736	60.0843	1.610005	1.610005	0.974285	97.42853
SO ₃	0.311	80.0632	0.003884	-	-	-
TiO ₂	2.319	79.8658	0.029036	0.029036	0.017571	1.75711
Fe ₂ O ₃	0.038	159.6922	0.000238	0.000476	0.000288	0.0288

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จุฬาลงกรณ์มหาวิทยาลัย

Table B5 Calculated composition of Al-TS-1 (127).

Al-TS-1 (127)			mole of metal oxide	mole of cation	mole % of cation	Mol %
Compound	% wt	MW				
Al ₂ O ₃	0.644	101.9613	0.006316	0.012632	0.007683	0.7683
SiO ₂	96.176	60.0843	1.600684	1.600684	0.973545	97.35451
SO ₃	0.715	80.0632	0.008930	-	-	-
TiO ₂	2.426	79.8658	0.030376	0.030376	0.018475	1.847482
Fe ₂ O ₃	0.039	159.6922	0.000244	0.000488	0.000297	0.029707

Table B6 Calculated composition of Al-TS-1 (69).

Al-TS-1 (69)			mole of metal oxide	mole of cation	mole % of cation	Mol %
Compound	% wt	MW				
Al ₂ O ₃	1.19	101.9613	0.011671	0.023342	0.014069	1.406897
SiO ₂	96.687	60.0843	1.609189	1.609189	0.969902	96.99016
TiO ₂	2.074	79.8658	0.025969	0.025969	0.015652	1.565195
Fe ₂ O ₃	0.05	159.6922	0.000313	0.000626	0.000377	0.037743

ศูนย์วิทยทรัพยากร
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APPENDIX C

DATA OF CALCULATION OF ACID SITE

Table C1 Data from fityk programme.

Sample	Area		
	Weak acid strength	Medium acid strength	Strong acid strength
TS-1	0.01484	0.00331	-
AI-TS-1 (206)	0.00934	0.02332	0.00406
AI-TS-1 (166)	0.03302	0.00189	0.02275
AI-TS-1 (127)	0.04339	0.00216	0.03534
AI-TS-1 (69)	0.05485	0.00367	0.05137

Calculation of total acid sites

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

1. Calculation of total peak area to peak volume

From Figure F1 below, the volume of NH_3 calculates from equation $y = 69.652x$.

$$\begin{aligned}
 \text{The volume of NH}_3 &= 69.652 \times \text{area} \\
 \text{(Weak acid strength)} &= 69.652 \times 0.01484 \\
 &= 1.0338 \text{ ml}
 \end{aligned}$$

$$\begin{aligned}
 \text{The volume of NH}_3 &= 69.652 \times \text{area} \\
 \text{(Medium acid strength)} &= 69.652 \times 0.00331 \\
 &= 0.2304 \text{ ml}
 \end{aligned}$$

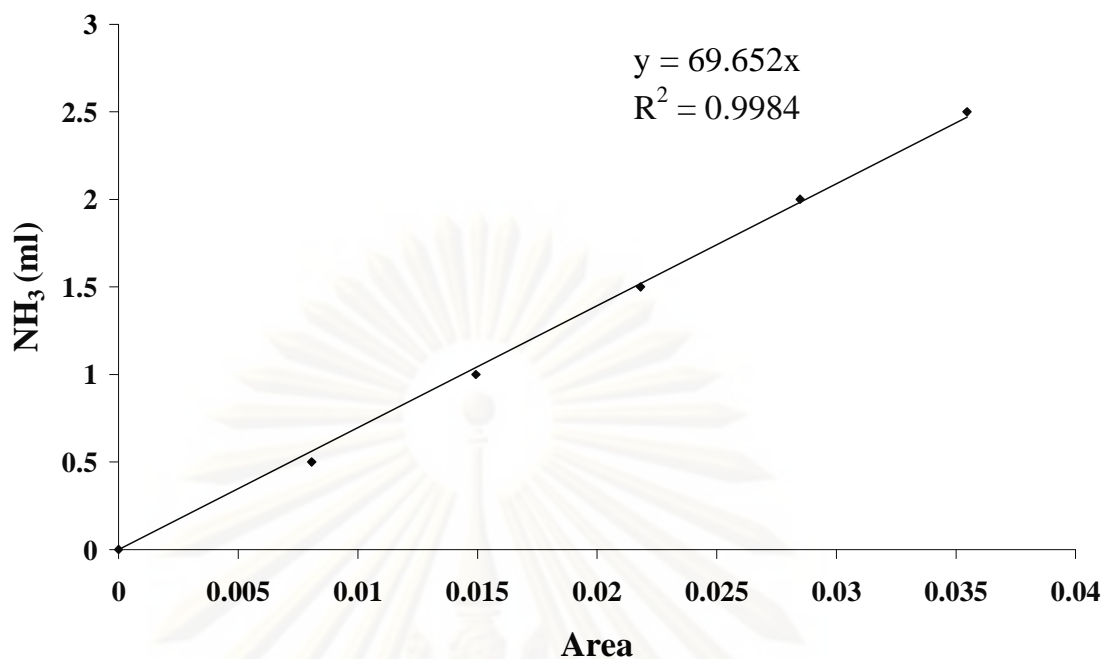


Figure C1 The calibration curve of ammonia.

2. Calculation for adsorbed volume of 15% NH₃

$$\begin{aligned}
 \text{Adsorbed volume of 15\% NH}_3 &= 0.15 \times \text{total peak volume} \\
 \text{(Weak acid strength)} &= 0.15 \times 1.0338 \text{ ml} \\
 &= 0.1551 \text{ ml}
 \end{aligned}$$

$$\begin{aligned}
 \text{Adsorbed volume of 15\% NH}_3 &= 0.15 \times \text{total peak volume} \\
 \text{(Medium acid strength)} &= 0.15 \times 0.2304 \text{ ml} \\
 &= 0.0346 \text{ ml}
 \end{aligned}$$

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จุฬาลงกรณ์มหาวิทยาลัย

3. The acid sites are calculated from the following equation

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

For TS-1 sample, 0.1003 g of this sample was measured, therefore

$$\begin{aligned} \text{The acid sites (Weak acid strength)} &= \frac{0.1551 \text{ ml} \times 101.325 \text{ Pa}}{8.314 \times 10^{-3} \frac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}} \times 298 \text{ K} \times 0.1003 \text{ g}} \\ &= 63.2306 \mu\text{mol/g} \end{aligned}$$

$$\begin{aligned} \text{The acid sites (Medium acid strength)} &= \frac{0.0346 \text{ ml} \times 101.325 \text{ Pa}}{8.314 \times 10^{-3} \frac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}} \times 298 \text{ K} \times 0.1003 \text{ g}} \\ &= 14.0935 \mu\text{mol/g} \end{aligned}$$

$$\begin{aligned} \text{The total acid sites} &= 63.2306 + 14.0935 \\ &= 77 \mu\text{mol/g} \end{aligned}$$

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จุฬาลงกรณ์มหาวิทยาลัย

APPENDIX D

CALIBRATION CURVES

This appendix shows the calibration curves for calculation of products in the oxidation of toluene reaction. The main products are benzaldehyde, o-cresol and p-cresol.

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

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

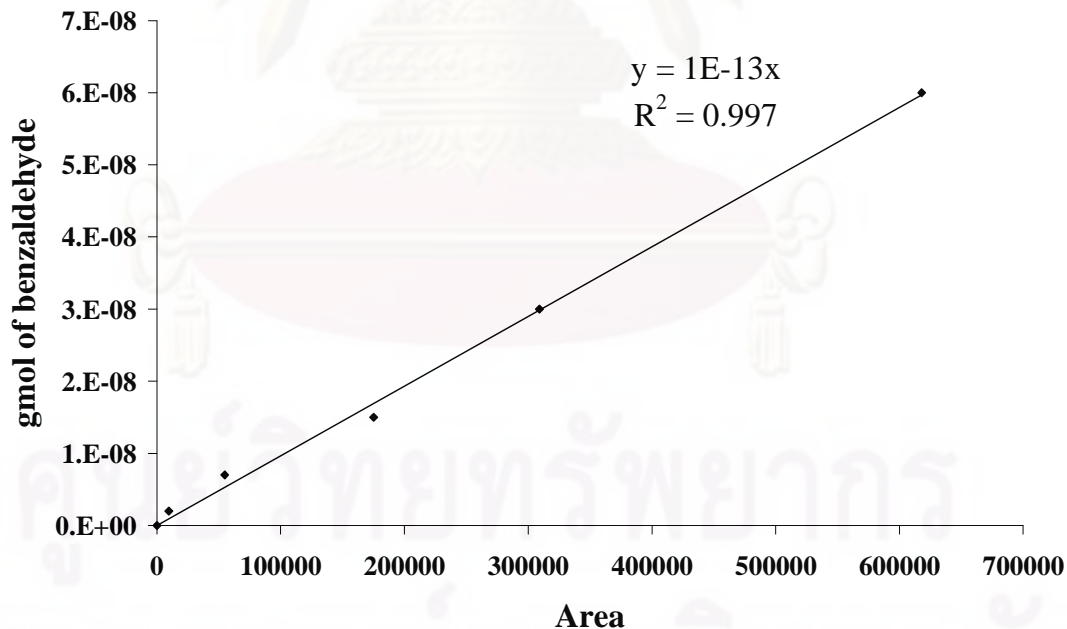


Figure D1 The calibration curve of benzaldehyde.

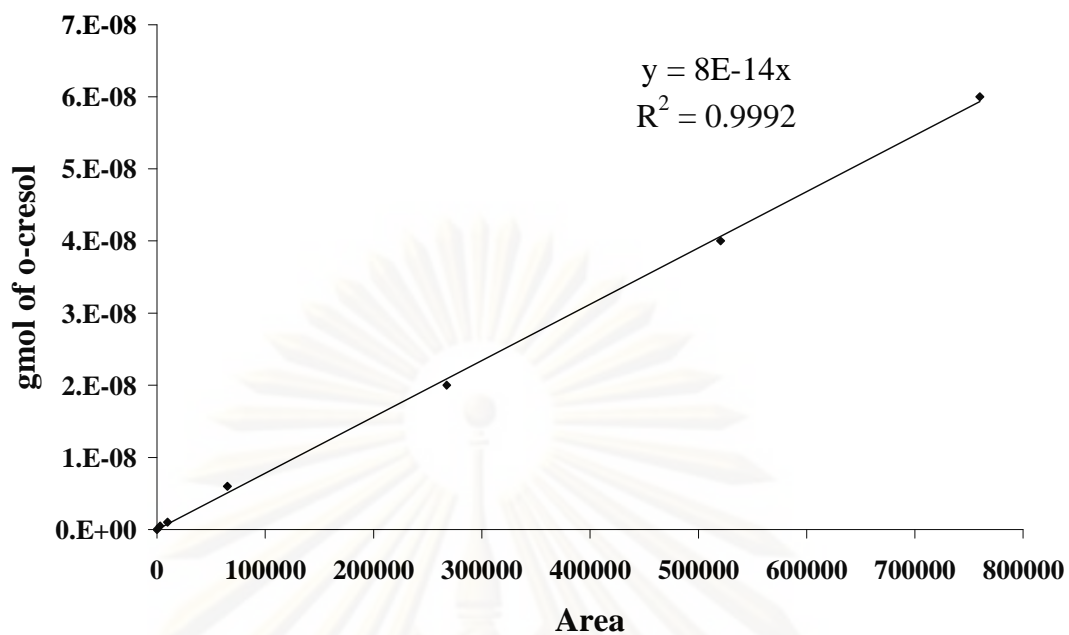


Figure D2 The calibration curve of o-cresol.

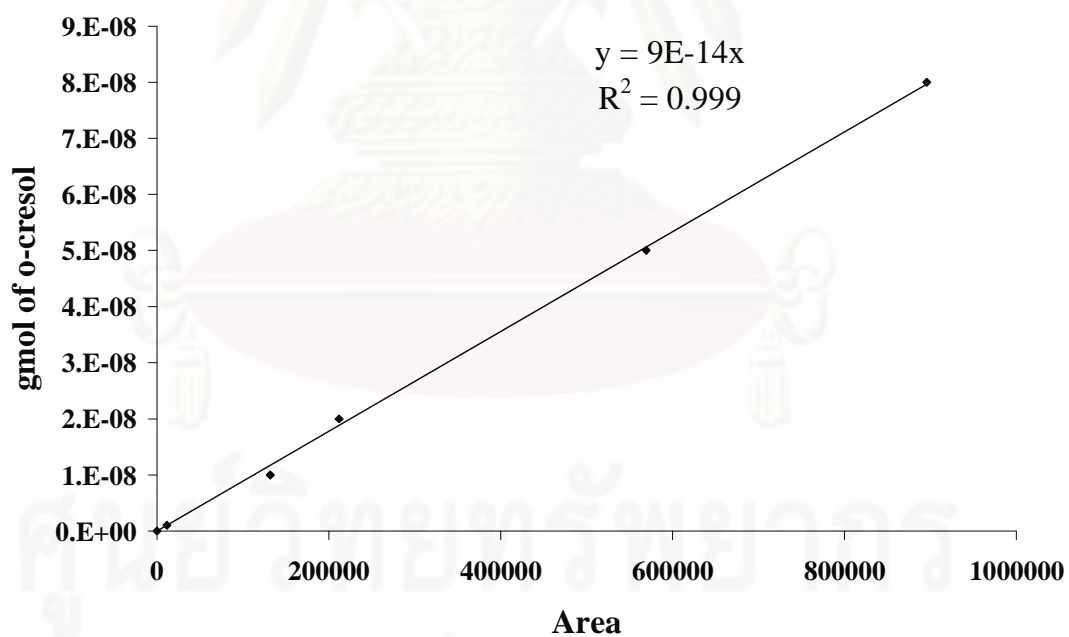


Figure D3 The calibration curve of p-cresol.

APPENDIX E

DATA OF EXPERIMENTS

Table E1 Data of Figure 4.8.

Catalysts	%H ₂ O ₂ convert to product	
	Reaction temperature	
	70 °C	110 °C
TS-1	0.88963	5.49364
Al-TS-1 (206)	1.31596	1.94118
Al-TS-1 (166)	2.26058	5.65596
Al-TS-1 (127)	8.55837	12.37490
Al-TS-1 (69)	5.16742	17.01873

Table E2 Data of Figure 4.9.

Catalysts	Productivity					
	Reaction temperature					
	70 °C			110 °C		
	Benzal- dehyde	o-Cresol	p-Cresol	Benzal- dehyde	o-Cresol	p-Cresol
TS-1	0.77370	0.53916	0.81523	6.39886	1.87489	3.23943
Al-TS-1 (206)	1.66554	0.38363	0.57943	3.02061	0.18869	0.10376
Al-TS-1 (166)	3.26236	0.51910	0.33122	8.85425	0.53562	0.20823
Al-TS-1 (127)	11.86933	1.13958	3.05148	18.24496	0.72569	3.17720
Al-TS-1 (69)	7.07841	0.30056	2.39775	23.20398	8.86424	0.26738

Table E3 Data of Figure 4.10.

Catalysts	%Selectivity					
	Reaction temperature					
	70 °C			110 °C		
	Benzal- dehyde	o-Cresol	p-Cresol	Benzal- dehyde	o-Cresol	p-Cresol
TS-1	53.32571	18.58023	28.09407	71.44759	10.46723	18.08519
Al-TS-1 (206)	77.57280	8.93374	13.49346	95.38260	2.97924	1.63817
Al-TS-1 (166)	88.47022	7.03865	4.49113	95.96885	2.90270	1.12845
Al-TS-1 (127)	84.99424	4.08019	10.92558	90.33766	1.79658	7.86576
Al-TS-1 (69)	83.99118	1.78320	14.22563	83.55837	15.96022	0.48142

Table E4 Data of Figure 4.11.

Catalysts	%H ₂ O ₂ convert to product	
	Reaction temperature	
	110 °C	120 °C
TS-1	5.49364	8.46293
Al-TS-1 (206)	1.94118	12.78700
Al-TS-1 (166)	5.65596	12.49680
Al-TS-1 (127)	12.37490	17.36658
Al-TS-1 (69)	17.01873	14.48783

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จุฬาลงกรณ์มหาวิทยาลัย

Table E5 Data of Figure 4.12.

Catalysts	Productivity					
	Reaction temperature					
	110 °C			120 °C		
	Benzal- dehyde	o-Cresol	p-Cresol	Benzal- dehyde	o-Cresol	p-Cresol
TS-1	6.39886	1.87489	3.23943	11.98421	1.36884	2.28376
Al-TS-1 (206)	3.02061	0.18869	0.10376	18.87931	1.01342	2.96171
Al-TS-1 (166)	8.85425	0.53562	0.20823	18.55326	0.80812	2.87200
Al-TS-1 (127)	18.24496	0.72569	3.17720	25.02589	0.90127	5.72739
Al-TS-1 (69)	23.20398	8.86424	0.26738	20.68796	0.33793	5.56160

Table E6 Data of Figure 4.13.

Catalysts	%Selectivity					
	Reaction temperature					
	110 °C			120 °C		
	Benzal- dehyde	o-Cresol	p-Cresol	Benzal- dehyde	o-Cresol	p-Cresol
TS-1	71.44759	10.46723	18.08519	86.77603	4.95578	8.26819
Al-TS-1 (206)	95.38260	2.97924	1.63817	90.47503	2.42829	7.09668
Al-TS-1 (166)	95.96885	2.90270	1.12845	90.97713	1.98134	7.04152
Al-TS-1 (127)	90.33766	1.79658	7.86576	88.30522	1.59008	10.10470
Al-TS-1 (69)	83.55837	15.96022	0.48142	87.52095	0.71481	11.76424

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Table E7 Data of Figure 4.14.

Catalysts	%H ₂ O ₂ convert to product	
	Reaction temperature	
	110 °C	120 °C
TS-1	8.63215	10.40548
Al-TS-1 (206)	13.77061	18.27836
Al-TS-1 (166)	21.59747	11.54996
Al-TS-1 (127)	15.44367	17.02193
Al-TS-1 (69)	18.32534	19.45038

Table E8 Data of Figure 4.15.

Catalysts	Productivity					
	Reaction temperature					
	110 °C			120 °C		
	Benzal- dehyde	o-Cresol	p-Cresol	Benzal- dehyde	o-Cresol	p-Cresol
TS-1	10.13766	2.67982	5.20971	13.94079	2.05754	4.00158
Al-TS-1 (206)	19.90782	1.51960	3.59084	26.62170	1.99075	4.39827
Al-TS-1 (166)	30.45323	8.21439	1.32594	17.61118	0.63121	1.84659
Al-TS-1 (127)	21.96610	6.30708	0.13500	24.47764	1.29285	5.27412
Al-TS-1 (69)	26.79784	5.53553	0.64252	27.56824	6.32085	1.96072

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จุฬาลงกรณ์มหาวิทยาลัย

Table E9 Data of Figure 4.16.

Catalysts	%Selectivity					
	Reaction temperature					
	110 °C			120 °C		
	Benzal- dehyde	o-Cresol	p-Cresol	Benzal- dehyde	o-Cresol	p-Cresol
TS-1	71.98801	9.51477	18.49722	82.14792	6.06217	11.78991
Al-TS-1 (206)	88.62479	3.38245	7.99277	89.28600	3.33836	7.37564
Al-TS-1 (166)	86.45740	11.66042	1.88218	93.42762	1.67429	4.89809
Al-TS-1 (127)	87.21156	12.52043	0.26800	88.17236	2.32853	9.49911
Al-TS-1 (69)	89.66426	9.26081	1.07492	86.94131	9.96695	3.09174

Table E10 Data of Figure 4.17.

Catalysts	%H ₂ O ₂ convert to product	
	Molar ratio H ₂ O ₂ : toluene	
	1:1	2:1
TS-1	5.49364	8.63215
Al-TS-1 (206)	1.94118	13.77061
Al-TS-1 (166)	5.65596	21.59747
Al-TS-1 (127)	12.37490	15.44367
Al-TS-1 (69)	17.01873	18.32534

Table E11 Data of Figure 4.18.

Catalysts	Productivity					
	Molar ratio H ₂ O ₂ : toluene					
	1:1			2:1		
	Benzal- dehyde	o-Cresol	p-Cresol	Benzal- dehyde	o-Cresol	p-Cresol
TS-1	6.39886	1.87489	3.23943	10.13969	2.68036	5.21076
Al-TS-1 (206)	3.02061	0.18869	0.10376	19.90782	1.51960	3.59084
Al-TS-1 (166)	8.85425	0.53562	0.20823	30.45323	8.21439	1.32594
Al-TS-1 (127)	18.24496	0.72569	3.17720	21.96610	6.30708	0.13500
Al-TS-1 (69)	23.20398	8.86424	0.26738	26.79784	5.53553	0.64252

Table E12 Data of Figure 4.19.

Catalysts	%Selectivity					
	Molar ratio H ₂ O ₂ : toluene					
	1:1			2:1		
	Benzal- dehyde	o-Cresol	p-Cresol	Benzal- dehyde	o-Cresol	p-Cresol
TS-1	71.44759	10.46723	18.08519	71.98801	9.51477	18.49722
Al-TS-1 (206)	95.38260	2.97924	1.63817	88.62479	3.38245	7.99277
Al-TS-1 (166)	95.96885	2.90270	1.12845	86.45740	11.66042	1.88218
Al-TS-1 (127)	90.33766	1.79658	7.86576	87.21156	12.52043	0.26800
Al-TS-1 (69)	83.55837	15.96022	0.48142	89.66426	9.26081	1.07492

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Table E13 Data of Figure 4.20.

Catalysts	%H ₂ O ₂ convert to product	
	Molar ratio H ₂ O ₂ : toluene	
	1:1	2:1
TS-1	8.46293	10.40548
Al-TS-1 (206)	12.78700	18.27836
Al-TS-1 (166)	12.49680	11.54996
Al-TS-1 (127)	17.36658	17.02193
Al-TS-1 (69)	14.48783	19.45038

Table E14 Data of Figure 4.21.

Catalysts	Productivity					
	Molar ratio H ₂ O ₂ : toluene					
	1:1			2:1		
	Benzal- dehyde	o-Cresol	p-Cresol	Benzal- dehyde	o-Cresol	p-Cresol
TS-1	11.98421	1.36884	2.28376	13.94079	2.05754	4.00158
Al-TS-1 (206)	18.87931	1.01342	2.96171	26.62170	1.99075	4.39827
Al-TS-1 (166)	18.55326	0.80812	2.87200	17.61118	0.63121	1.84659
Al-TS-1 (127)	25.02589	0.90127	5.72739	24.47764	1.29285	5.27412
Al-TS-1 (69)	20.68796	0.33793	5.56160	27.56824	6.32085	1.96072

Table E15 Data of Figure 4.22.

Catalysts	%Selectivity					
	Molar ratio H ₂ O ₂ : toluene					
	1:1			2:1		
	Benzal- dehyde	o-Cresol	p-Cresol	Benzal- dehyde	o-Cresol	p-Cresol
TS-1	86.77603	4.95578	8.26819	82.14792	6.06217	11.78991
Al-TS-1 (206)	90.47503	2.42829	7.09668	89.28600	3.33836	7.37564
Al-TS-1 (166)	90.97713	1.98134	7.04152	93.42762	1.67429	4.89809
Al-TS-1 (127)	88.30522	1.59008	10.10470	88.17236	2.32853	9.49911
Al-TS-1 (69)	87.52095	0.71481	11.76424	86.94131	9.96695	3.09174

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APPENDIX F**MATERIAL SAFETY DATA SHEET****Toluene****General**

Synonyms : ethenylmethylbenzene, tolylethylene, NCI-C56406, vinyltoluene,
1-methyl-1-phenylethylene

Molecular formula : C₉H₁₀

Physical data

Appearance	: colourless liquid with a strong and unpleasant odour
Melting point	: -70 to -75 °C
Boiling point	: 170 °C
Vapour density	: 4.1 (air = 1)
Density (g cm ⁻³)	: 0.903
Flash point	: 54 °C
Explosion limits	: 1.9 - 6.1 %
Water solubility	: negligible

Stability

Stable. Flammable. Incompatible with oxidizing agents, peroxides, strong acids, aluminium chloride. May contain small amounts of t-butylcatechol to inhibit polymerization.

Toxicology

Harmful if swallowed or inhaled. Chronic exposure may lead to liver or kidney damage. Experimental teratogen.

Personal protection

Safety glasses, good ventilation.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Hydrogen peroxide

General

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

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

Molecular formula : H_2O_2

Physical data

Appearance	: colourless liquid
Melting point	: -28 °C
Boiling point	: 114 °C
Specific gravity	: typically near 1.19
Vapour pressure	: 23.3 at 30 °C

Stability

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

Toxicology

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

Hazards Identification

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

Potential Health Effects

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

Ingestion : Corrosive and irritating to the mouth, throat, and abdomen. Large doses may cause symptoms of abdominal pain, vomiting, and diarrhea as well as blistering or tissue destruction. Stomach distention (due to rapid liberation of oxygen), and risk of stomach perforation, convulsions, pulmonary edema, coma, possible cerebral edema (fluid on the brain), and death are possible.

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

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

Personal protection

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

***o*-Cresol**

General

Synonyms : 2-cresol, *o*-cresylic acid, 1-hydroxy-2-methylbenzene, *o*-methylphenol, 2-methylphenol, *o*-toluol, 2-hydroxytoluene, *o*-hydroxytoluene

Molecular formula : C₇H₈O

Physical data

Appearance : colourless to light yellow liquid

Melting point : 32 - 34 °C

Boiling point : 191 °C

Vapour pressure : 0.3 mm Hg at 20 °C

Specific gravity : 1.048

Flash point : 81 °C

Autoignition temperature : 598 °C

Stability

Stable, but light and air sensitive. Combustible. Incompatible with oxidizing agents, bases.

Toxicology

Highly toxic. May be fatal if inhaled, swallowed or absorbed through skin. Experimental neoplastigen. Human mutagenic data. Readily absorbed through the skin. Very destructive of mucous membranes. Causes burns. Inhalation may cause spasm. Severe skin and eye irritant.

Personal protection

Safety glasses, gloves, good ventilation.

***p*-Cresol**

General

Synonyms : 1-hydroxy-4-methylbenzene, 4-methylphenol, *p*-cresylic acid, 4-cresol, *p*-hydroxytoluene, 4-hydroxytoluene, *p*-methylphenol, para-cresol, *p*-tolyl alcohol, *p*-toluol

Molecular formula : $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$

Physical data

Appearance	: crystals
Melting point	: 34 °C
Boiling point	: 202 °C
Vapour pressure	: 0.1 mm Hg at 20 °C
Density (g cm^{-3})	: 1.03
Flash point	: 86 (closed cup)
Water solubility	: moderate

Stability

Stable. Combustible. Incompatible with strong oxidizing agents. Air and light-sensitive. Hygroscopic.

Toxicology

Poison. May be fatal if swallowed. Readily absorbed through the skin. Harmful if swallowed or inhaled, and in contact with skin. Corrosive - causes severe burns. May cause serious eye damage. Severe skin and eye irritant.

Personal protection

Safety glasses, gloves, adequate ventilation.

Benzaldehyde

General

Synonyms : benzoic aldehyde, almond artificial essential oil, benzenecarbonal, benzene carboxaldehyde, artificial almond oil, NCI-C56133, oil of bitter almond

Molecular formula : C_6H_5CHO

Physical data

Appearance	: colourless to yellow liquid with an almond-like odour
Melting point	: $-56\text{ }^{\circ}\text{C}$
Boiling point	: $179\text{ }^{\circ}\text{C}$
Vapour density	: 3.6 (air = 1)
Vapour pressure	: 1 mm Hg at $26\text{ }^{\circ}\text{C}$
Density (g cm^{-3})	: 1.04
Flash point	: $63\text{ }^{\circ}\text{C}$ (closed cup)
Explosion limits	: 2.1 - 13.5 %
Autoignition temperature	: $192\text{ }^{\circ}\text{C}$
Water solubility	: slight

Stability

Stable. Combustible. Incompatible with strong oxidizing agents, strong acids, reducing agents, steam. Air, light and moisture-sensitive.

Toxicology

Eye irritant. Harmful by inhalation or ingestion. May be harmful by skin contact. May cause allergic reaction. Slight local anesthetic properties. There is limited evidence that this chemical may act as a carcinogen in laboratory animals. Narcotic in high concentration.

Personal protection

Safety glasses, adequate ventilation.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Titanium (IV) n-butoxide

General

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

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

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

Physical data

Boiling point : 310-314 °C

Flash point : 78 °C

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

Toxicology

Irritating to eyes, respiratory system and skin.

Personal protection

Avoid contact with skin and eyes.

Tetrapropylammonium bromide

General

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

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

Chemical formula : $(C_3H_7)_4NBr$

Physical data

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

Stability and reactivity

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

Hazardous decomposition

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

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Potential health effect

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

First aid measure

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

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

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

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

Fire fighting measures

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

Hazardous product combustion

May emit Nitrogen oxides, Hydrobromic acid and Carbon monoxide.

Sodium chloride

General

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

Molecular formula : NaCl

Physical data

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

Stability

Stable. Incompatible with strong oxidizing agents.

Toxicology

May cause skin, eye or respiratory irritation.

Personal protection

Not believed to present a significant hazard to health.

Sodium hydroxide

General

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

Molecular formula: NaOH

Physical data

Appearance : colorless white solid (often sold as pellets)

Melting point : 318 °C

Boiling point : 1,390 °C

Vapor pressure : 1 mm Hg at 739 °C

Specific gravity (g cm⁻³) : 2.12

Water solubility : high

Stability

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

Toxicology

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

Personal protection

Safety glasses, adequate ventilation, Neoprene or PVC gloves.

Sodium silicate

General

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

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

Physical data

Appearance : colourless liquid as usually supplied (solution)
Boiling point : ca. 102 °C for a 40% aqueous solution
Specific gravity : approximately 1.3 for a ca. 40% solution

Stability

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

Toxicology

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

Personal protection

Safety glasses, gloves.

Aluminium (III) nitrate nonahydrate

General

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

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

Physical data

Appearance : white crystalline powder

Melting point : 73 °C

Water solubility : appreciable

Stability

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

Toxicology

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

Personal protection

Safety glasses, adequate ventilation.

Ethanol

General

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

Molecular formula : C_2H_5OH

Physical data

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

Stability

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

Toxicology

Causes skin and eye irritation. Ingestion can cause nausea, vomiting and inebriation; chronic use can cause serious liver damage. Note that "absolute" alcohol, which is close to 100% ethanol, may nevertheless contain traces of 2-propanol, together with methanol or benzene. The latter two are very toxic, while "denatured" alcohol has substances added to it which make it unpleasant and possibly hazardous to consume.

Personal protection

Safety glasses. Suitable ventilation.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

VITA



Mr. Viriya Siridumrongdej was born on November 25th, 1985 in Bangkok, Thailand. He finished high school from Suankularb wittayalai School in 2004, and received the bachelor's degree of Chemical Engineering from Faculty of Engineer, Mahidol University in 2008. He continued his master's study at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University in June, 2008.

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ศูนย์วิจัยทรัพยากร
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