การสังเคราะห์เบนซัลดีไฮด์จากโทลูอีนในปฏิกิริยาขั้นตอนเดียว

นางสาวภัทราพร หาญวานิช

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2551

DIRECT SYNTHESIS OF BENZALDEHYDE FROM TOLUENE

Ms. PATTARAPORN HARNVANICH

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic year 2008

Thesis Title DIRECT SYNTHESIS OF BENZALDHYDE FROM TOLUENE

By Miss. Pattaraporn Harnvanich
Field of Study Chemical Engineering
Thesis Advisor Associate Professor Tharathon Mongkhonsi, Ph.D.

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

....Dean of the Faculty of Engineering
(Associate Professor Boonsom Lerdhirunwong, Dr.Ing.)

THESIS COMMITTEE

.... Chairman
(Assistant Professor Anongnat Somwangthanaroj, Ph.D.)

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

.........Soorathep Kheawhom........ Examiner
(Soorathep Kheawhom, Ph.D.)

.........Kriangsak Kraiwattanawong........ External Examiner
(Kriangsak Kraiwattanawong, D.Eng.)

ภัทราพร หาญวานิช: การสังเคราะห์เบนซัลดีไฮด์จากโทลูอีนในปฏิกิริยาขั้นตอนเดียว (DIRECT SYNTHESIS OF BENZALDEHYDE FROM TOLUENE) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.ธราธร มงคลศรี, 107 หน้า

งานวิจัยนี้ทำการศึกษาการสังเคราะห์เบนซัลดีไฮด์โดยตรงจากโทลูอีนร่วมกับไฮโดรเจนเปอร์ออกไซด์ โดยมีตัวเร่งปฏิกิริยาไทเทเนียมซิลิกาไลต์-1 ที่ได้รับการปรับปรุงด้วยโลหะอะลูมิเนียมในปริมาณต่าง ๆ ที่อุณหภูมิการทำปฏิกิริยา 70 และ 90 องศาเซลเซียส และอัตราส่วนโดยโมลของสารตั้งต้นระหว่างโทลูอีนและไฮโดรเจนเปอร์ออกไซด์เป็น 1:1 และ 2:1 ผลการศึกษาพบว่าตัวเร่งปฏิกิริยาที่ได้รับการปรับปรุงทุกตัวให้ผลิตภัณฑ์หลักเป็นเบนซัลดีไฮด์ โดยมีออโธ-ครีซอลและพารา-ครีซอล เป็นผลิตภัณฑ์ข้างเคียง ผลการทดลองแสดงให้เห็นว่าอะลูมิเนียมที่เติมเข้าไปในตัวเร่งปฏิกิริยาไทเทเนียมซิลิกาไลต์-1 จะเพิ่มการเกิดเบนซัลดีไฮด์และยับยั้งการเกิดครีซอล แต่ถ้าเติมในปริมาณที่มากเกินไปจะทำให้ความว่องไวของตัวเร่งปฏิกิริยาลดลง ค่าการเลือกเกิดเบนซัลดีไฮด์จะสูงขึ้นเมื่ออุณหภูมิการทำปฏิกิริยาเพิ่มสูงขึ้น แต่ถ้าเพิ่มสัดส่วนของโทลูอีนต่อไฮโดรเจนเปอร์ออกไซด์ให้สูงขึ้นจะทำให้ค่าการเลือกเกิดเบนซัลดีไฮด์ลดลง ทั้งนี้เป็นเพราะโทลูอีนจะไปปกคลุมพื้นผิวของตัวเร่งปฏิกิริยา ทำให้ปริมาณไฮโดรเจนเปอร์ออกไซด์บนพื้นผิวลดลง ปฏิกิริยาการเกิดเบนซัลดีไฮด์ซึ่งต้องใช้ไฮโดรเจนเปอร์ออกไซด์มากกว่าปฏิกิริยาการเกิดครีซอลถึง 2 เท่าจึงลดลงตามไปด้วย

ภาควิชา.............วิศวกรรมเคมี.......... ลายมือชื่อนิสิต ......ภัทราพร หาญวานิช......................
สาขาวิชา............วิศวกรรมเคมี.......... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....
ปีการศึกษา..........2551....................

##5070393521: MAJOR CHEMICAL ENGINEERING

KEYWORDS: ALUMINIUM TITANIUM SILICALITE-1/ TOLUENE/ STIRRED REACTOR/ HYDROXYLATION

PATTARAPORN HARNVANICH: DIRECT SYNTHESIS OF BENZALDEHDYE FROM TOLUENE. ADVISOR: ASSOC.PROF. THARATHON MONGKHONSI, Ph.D., 107 pp.

This research studied the direct synthesis of benzaldehyde from toluene and hydrogen peroxide using titanium silicalite-1 catalysts modified with different amount of Al. 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. It is found that all modified catalysts yield benzaldehyde as the major product with o-cresol and p-cresol as by products. The experimental results also show that Al added into TS-1 promotes the formation of benzaldehyde and suppresses the formation of cresols. Too much Al added, however, will decrease the catalytic activity of the modified catalysts. Benzaldehyde selectivity increases with the increase in reaction temperature. On the contrary, benzaldehyde selectivity decreases if toluene per hydrogen peroxide molar ratio is increased from 1:1 to 2:1. This is due to toluene will cover the catalyst surface, leaving lesser hydrogen peroxide on the catalyst surface. The formation of benzaldehyde which requires twice amount of hydrogen peroxide than the formation of cresol, therefore, decreases.

Department:...Chemical Engineering... Student's Signature....ภัทราพร...หาญวานิช....
Field of Study: .Chemical Engineering... Advisor's Signature..........................
Academic Year.....2008.....................

ACKNOWLEDGEMENTS

I am sincerely grateful to my advisor, Associate Professor Tharathon Mongkhonsi, for his invaluable guidance and value suggestions including constant encourage throughout this study. Furthermore, I deeply appreciate all the things, I have learnt from him and for the opportunity to work in his group, I really enjoyed our meetings and pleasure with my thesis. I am also grateful to Assistance Professor Anongnat Somwangthanaroj, as the chairman, Dr. Soorathep Kheawhom and Dr. Kriangsak Kraiwattanawong, who have been members of thesis committee.

I am thankful to my lab mates, Miss Phawana Wong boonrod, Miss Rojarek Passasadee and many friends in the process control laboratory for useful help. I want to especially thankful to Miss Dang Saebe for her constant supports and longer wonderful friendship, likewise Miss Pornapa Kasemsiri, Mr. Piyaphong Phromsalee, and Miss Charinya Phoameung for their encouragements and very nice time.

Finally, my deepest regard to my family, who have always been the source of my support and encouragement.

CONTENTS

Page

APPENDICES........

Page

LIST OF TABLES

TABLE Page

LIST OF FIGURE

CHAPTER I

INTRODUCTION

Benzaldehyde is a chemical compound consisting of a benzene ring with an aldehyde substituent. It is the simplest representative of the aromatic aldehydes and one of the most industrially used members of this family of compounds. At room temperature it is a colorless liquid with a characteristic and pleasant almond-like odor. Benzaldehyde is an important component of the scent of almonds, hence its typical odor. It is the primary component of bitter almond oil extract, and can be extracted from a number of other natural sources in which it occurs, such as apricot, cherry, and laurel leaves, peach seeds and, in a glycoside combined form (amygdalin), in certain nuts and kernels. It is used in manufacturing of benzoic acid, pharmaceuticals and dyes, as a solvent for oils, cellulose acetrate and nitrate.

Benzaldehyde can be obtained by many processes. Presently liquid phase chlorination or oxidation of toluene is among the most used processes. There are also a number of discontinued applications such as partial oxidation of benzyl alcohol alkali treating of benzal chloride and reaction between benzene and carbon monoxide. The chlorination of toluene (the old route) has to firstly toluene react with chlorine in 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. The direct oxidation of toluene also possesses the disadvantage of the over oxidation of toluene to benzoic acid.

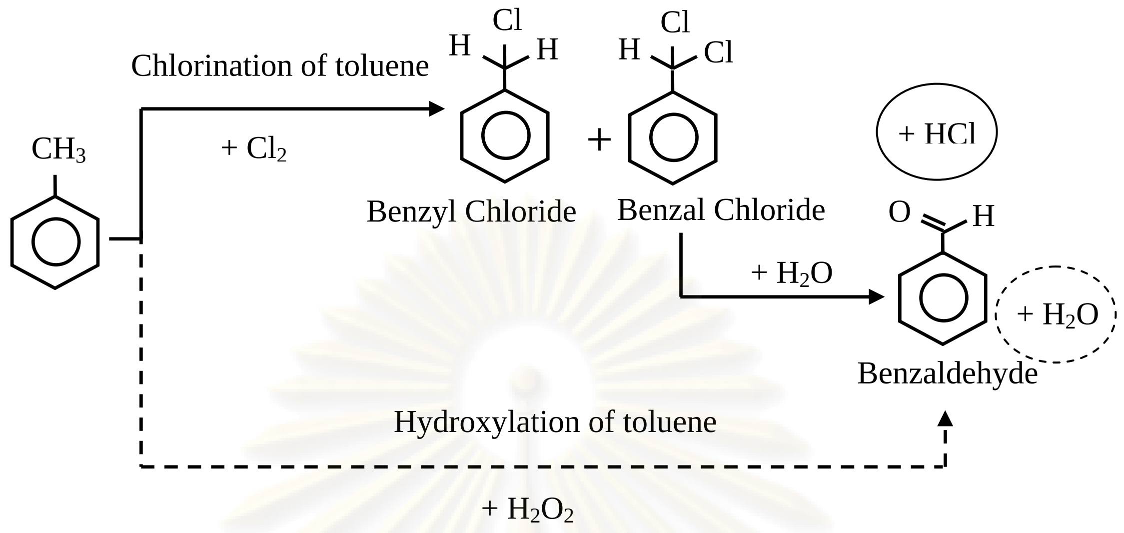


Figure 1.1 The synthesis route of benzaldehyde from toluene

The synthesis of titanium slicalite-1 (commonly known in the name TS-1) was firstly reported by Taramasso in 1983 opened new route of synthesis catalysis and catalytic reaction. 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.

Many researches focus on the hydroxylation reaction using hydrogen peroxide (H_2O_2) as oxidant. The use of H_2O_2 offers some advantages, such as low cost per oxygen atom and the absence of by-product. These reactions, because of the absence of by-product, are considered as “clean reaction”. A heterogeneous catalytic system has advantages over homogeneous systems since it allows simple separation and recovery of the catalyst from the reaction mixture and its subsequent regeneration, once it is deactivated. A direct catalytic method using heterogeneous, solid catalysts which can efficiently hydroxylate benzene, will have significant advantages and the titanium silicalite-1 (TS-1) catalyst have much more advantage than others. TS-1 has received interest in recent years because of its unique catalytic properties in oxidation involving hydrogen peroxide as the oxidant. TS-1 has the morphology and average pore size nearly same as ZSM-5. Thus the internal mass transfer is slow. Therefore, most of the reaction occurs at the external surface of the catalyst. The limiting step of this reaction should be the external mass transfer or the surface reaction. Consequently, the changing of the feeding system would affect the yield or selectivity of the reaction.

Therefore, the present work proposes a new route for the direct synthesis of benzaldehyde from toluene using H_2O_2 as oxidant and TS-1 (titanium silicalite-1) and Al-TS-1 as catalysts in a stirred slurry reactor. The research has been scoped as follows:

1) Synthesizing TS-1 and metal modified TS-1 catalysts (Al-TS-1) using incorporation technique to introduce second metal during hydrothermal synthesis.

2) The different ratio of synthesized catalysts 50 for Si/Ti and 50 100 150 200 for Si/Al.

3) Treatment of these catalysts with HNO_3 solution 5 M.

4) The synthesized catalysts will be characterized by using the following techniques.

- Determination of bulk composition of Si/Ti and Si/Ti by X-ray fluorescence (XRF).
- Determination of specific area by N_2 adsorption based on Brunaur-Emmett-Teller method (BET).
- Determination of phase structure and crystallinity of catalysts by X-ray diffractrometer (XRD).
- Determination of incorporation of Ti atoms as a framework element by Fourier-transform infrared spectroscopy (FT-IR).
- Determination of acid site and acid strength by temperature program desorption (TPD)

5) Investigate catalytic behavior of synthesized catalysts are evaluated by three phase hydroxylation of toluene using hydrogen peroxide as an oxidant in stirred slurry reactor with differences temperature reaction at 70°C and 90°C, and with difference molar ratio of reactant (toluene: H_2O_2) are 1: 1 and 2: 1.

This present work is organized as follows:

The background and scopes of the research are described in chapter I.

Chapter II fundamental theory concerning aromatic substitution and catalyst as TS-1 including reviews research works on the catalytic activity of metal modified TS-1 catalysts in the hydroxylation of aromatic compound.

Chapter III consists of catalyst preparation, catalyst characterization and catalytic reaction study in hydroxylation of toluene.

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

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

Finally, the sample of calculation of catalyst preparation and calibration curves from area to mole of reactants and products obtained from hydroxylation and data of the experiments which had 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-1(denoted TS-1) was discovered in 1983 by Tamasso. Catalyst, one of the most important innovations in heterogeneous catalysis over the last decades, is a high performances composite material specifically designed for industrial oxidation reactions with hydrogen peroxide.

Titanium silicalite is a crystalline zeotype material in which tetrahedral [TiO_4] and [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 from 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, 1997).

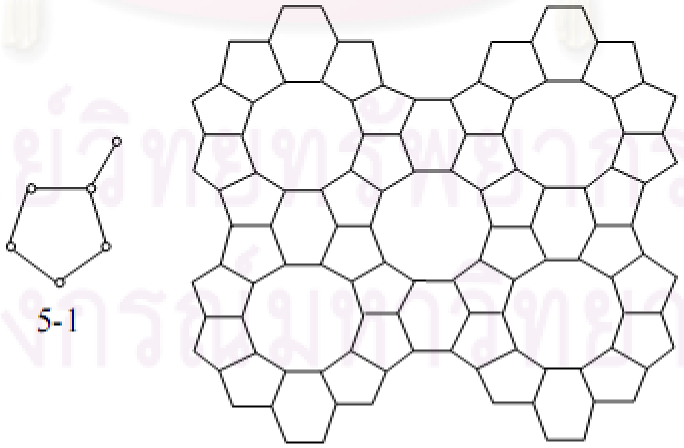


Figure 2.1 MFI structure (Tosheva L., 1999)

2.1.2 Application of TS-1

Since it is 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 from 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 sorms in many plants. The best known natural source of benzaldehyde is a mygdalin, in which it exists in a combinded from as a glycoside and which is present in bitter almonds. The odor bitter almonds arise from small amount of benzaldehyde formed by hydrolysis of the amygdalin. Owing to its occurrence in bitter alomonds, 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 product of benzaldehyde. It can be carried out either in an alkaline or in an acidic medium.

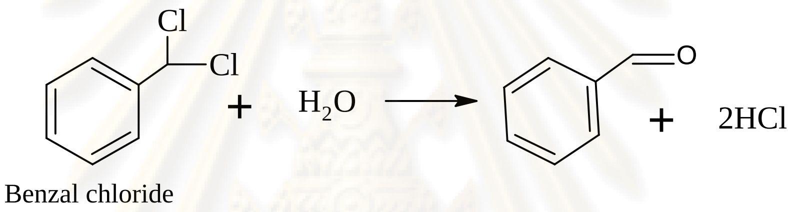


Figure 2.2 Hydrolysis of benzal chloride

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 is 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.

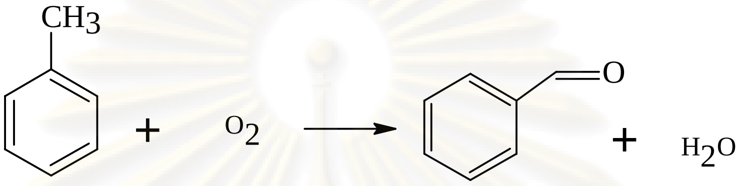


Figure 2.3 The oxidation of toluene

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 per sulfate, 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 2.3 below. The mechanism in figure 2.3 follows the generally accepted free radical substitution of halogen. The only difference is halogen atom (X•) is replaced by hydroxyl free radical (OH•). The initiating step is the breaking of O-O bond of the hydrogen peroxide 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 hydrogen peroxide to benzaldehyde (step 2 in figure 2.4)

Step 1

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

Step 2

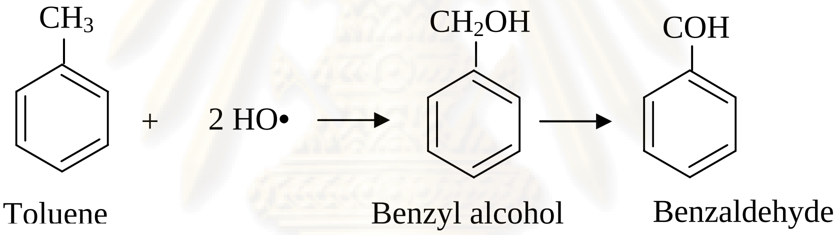


Figure 2.4 The mechanisms of benzaldehyde formation by hydroxyl free radical.

2.4 Electrophilic Aromatic substitution

The formation of cresol can be described by electrophilic aromatic substitution (EAS).

Above and below the plane of the benzene ring there is a cloud of π electrons showed below in figure 2.5. Through resonance, these π electrons are more involved in holding together carbon nuclei than are π electrons of a carbon – carbon double bond. Still, in comparison with σ electrons, these π electrons are loosely held and are available to a reagent that is seeking electrons. The benzene ring serves as a source of electrons, which is a base. The compounds with which it reacts are deficient in electrons, that is, are electrophile reagents or acids.

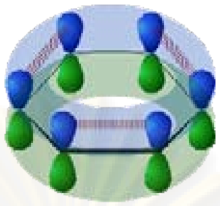
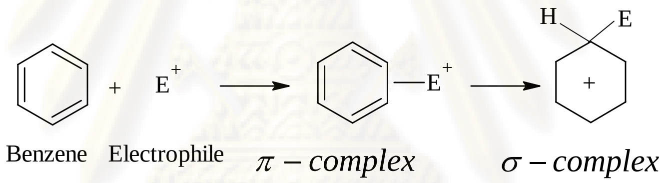


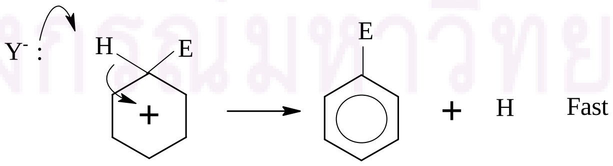
Figure 2.5 The pi electron cloud of benzene ring (www.chemgapedia.de/resonanz.vscml.html)

Electrophilic aromatic substitution generally takes the following form.

The first stage: The ring is attacked by electrophilic reagent to form carbocation.



The second stage: loss of a proton from the carbocation intermediate. Abstraction of proton to regain aromaticity and gives substituted product. Here we've introduced a new ion, Y^-. A lone pair of electrons on Y^- forms a bond with the hydrogen atom at the top of the ring. That means that the pair of electrons joining the hydrogen onto the ring is not needed any more. These then moves down to plug the gap in the delocalized electrons, so restoring the delocalized ring of electrons which originally gave the benzene its special stability.



Notes: Formation of the carbocation, the rate-determining step, is highly endothermic because it forms a non-aromatic carbocation.

In electrophilic aromatic substitution, there are three possible disubstituted products: ortho, meta and para. The preference for ortho, meta and para attack by the electrophile is different for different group. The group that attack to occur chiefly at positions ortho and para is called and ortho, para director. The group that attack to occur chiefly at positions meta is called meta director.

2.4.1 Theory of reactivity

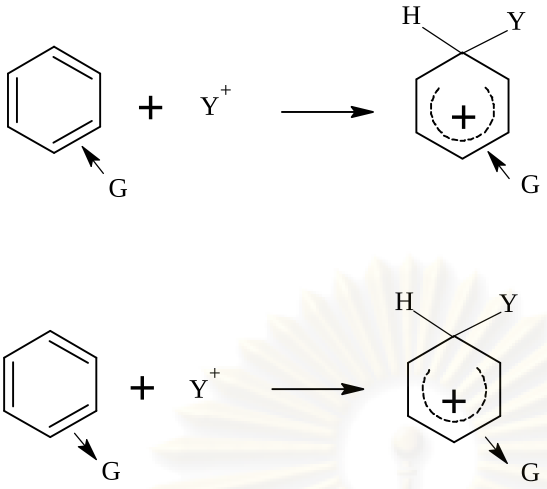
The activity of substituted benzene depends on type of substituent group. The group that releases electrons activates the ring is called “activating group”. The group that withdraws electrons deactivates the ring called “deactivating group”.

I. Activating groups

Activating groups release or donate electrons into the ring by a usually strong resonance effect. The π electrons flow from the substituents to the ring. The release of electrons into the ring stabilizes the positive charge that develops during the reaction, lowering the energy of activation, and increasing the reaction rate over that of benzene. The activating group direct incomes electrophiles to the ortho and para position of the ring.

II. Deactivating groups

Deactivating groups are electronegative and withdraw electrons from the ring by a strong resonance effect or by a strong inductive effect. The π electrons flow from the ring to the substutuents. The withdrawal of electrons from the ring destabilizes the positive charge that develops during the reaction, raising the energy of activation, and decreasing the reaction rate relative to benzene. Figure 2.6 shows type of substituent group.



G = release electrons:
stabilizes carbocation,
activates

G = withdraws electrons:
destabilizes carbocation,
deactivates

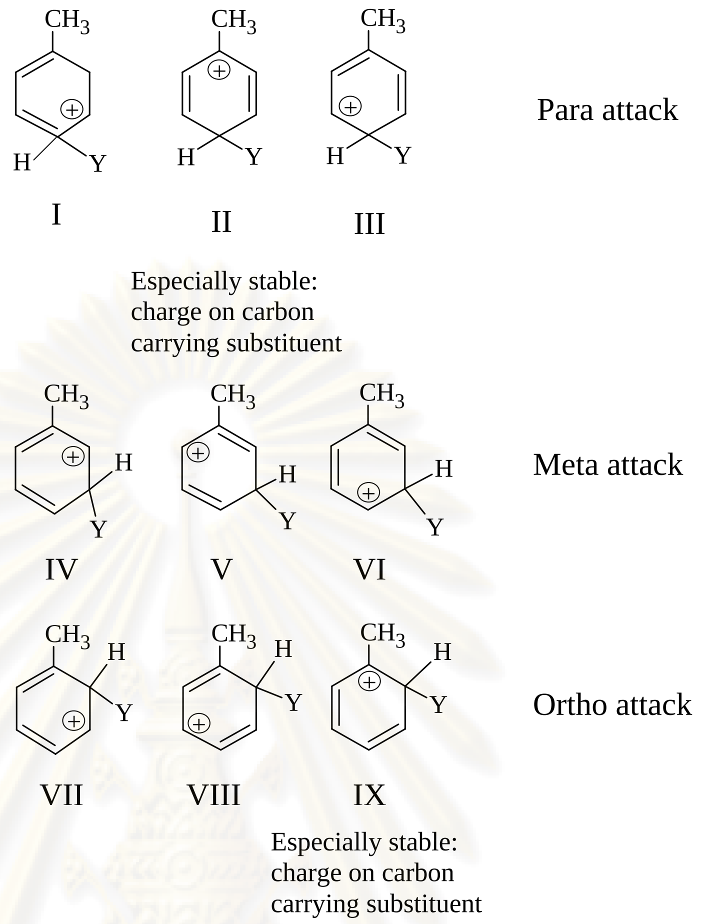
Figure 2.6 Type of substituent group in electrophilic aromatic substitution.

2.4.2 Theory of orientation

An activating group activates all position of the benzene ring; even the positions meta to it are more reactive than any single position in benzene itself. It directs ortho and para simply because it activates the ortho and para positions much more than it does the meta.

A deactivating group deactivates all positions in the ring, even the positions meta to it. It directs meta simply because it deactivates the ortho and para positions even more than it does the meta.

The carbocation formed by attack at the para and meta positions of toluene, a compound that contains an activating group. Each of these is a hybrid of three structures, I-III for para, IV – VI for meta. In the one of these six structures, II, the positive charge is located on the carbon atom to which CH_3 is attached. Although CH_3 releases electrons to all positions of the ring, it does so most strongly to the carbon atom nearest it; consequently, structure II is a particularly stable one. Because of contribution from structure II, the hybrid carbocation resulting from attack at the para position is more stable than the carbocation resulting from attack at a meta position. Para substitution, therefore, occur faster than meta substitution.



Especially stable:
charge on carbon
carrying substituent

Especially stable:
charge on carbon
carrying substituent

Figure 2.7 A Summary of substituent Effects in Electrophilic Substitutions

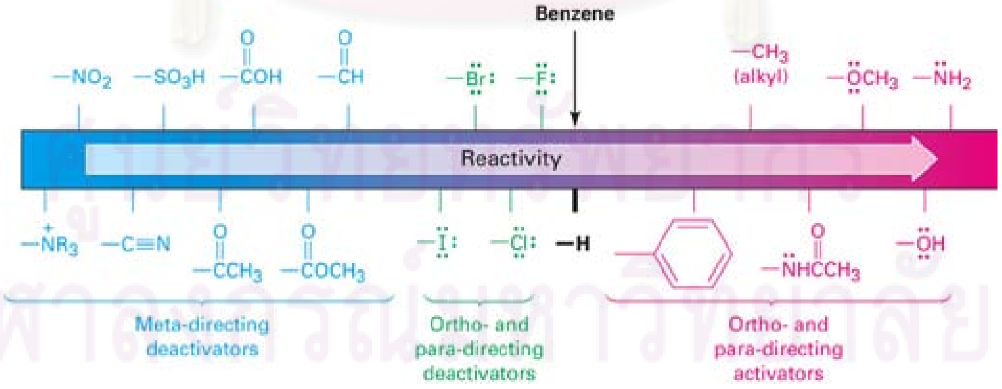


Figure 2.8 Classification of the various substituent groups.

(http://www.chem.umd.edu/courses/fall05/chem231fribush/pdfs/Chapter%2016.pdf)

2.5 Biphase and tri-phase catalysis

A large number of reactions are found not to occur or end up with very low reaction when the reactants are in different phase and the contact among the reactions is inhibited because of phase separation. This leads to poor mass transfer from one phase to the other, which results in very poor reaction.

The following three general types of tri-phase catalysis are most commonly observed.

(i) Liquid – Liquid – Solid
(ii) Solid – Liquid – Solid
(iii) Gas – Liquid – Solid.

In the liquid – liquid – solid (L-L-S) system, the reagent is usually present in the aqueous phase. In the solid- liquid-solid (S-L-S) type the reagent is usually present in the solid form. In the gas-liquid-solid (G-L-S) type, the reagent in the gaseous form is bubbled through the reactor. Since the essential requirement for a reaction to occur is the collision among the reactants, therefore the diffusion of the reactants is an extremely important phenomenon in the catalysis. It has been observed that tri-phase catalysis can also be made possible by suitable selection of the molecular sieves. When direct hydroxylation of simple aromatic compounds such as benzene, toluene, etc (liquid organic phase) was carried out with aqueous H_2O_2 as oxidant in the presence of excess amount of water (liquid aqueous phase, L) using solid micro porous TS -1 as catalyst (solid catalyst phase, S), a L-L-S system, a significant enhancement in both the reaction rates as well as product selectivity was observed. However, when an organic solvent such as methanol or acetone was used to homogenize the two immiscible liquid phases (solid – liquid phase, S-L type), the reaction was found to be very low. Schematically these phases are shown in figure 2. Although the similar types of diffusion reaction problems in the case of polymer supported resins can also be considered here, but unlike the former, here the competitive diffusion of the organic substrates compared to the water inside the relatively hydrophobic TS-1 should be considered. In this respect the TS-1 catalyzed tri-phase reaction differs from the former in that it’s the competitive diffusion of the organic substrates compared to water to the hydrophobic TS -1 channel is the controlling factor of the reaction. The same diffusion problems can also be considered in the case of bi-phase

(L-S) system also. Here the solvent, because of its smaller size, competes favorably than the organic substrates to diffuse into the hydrophobic channel of TS-1.

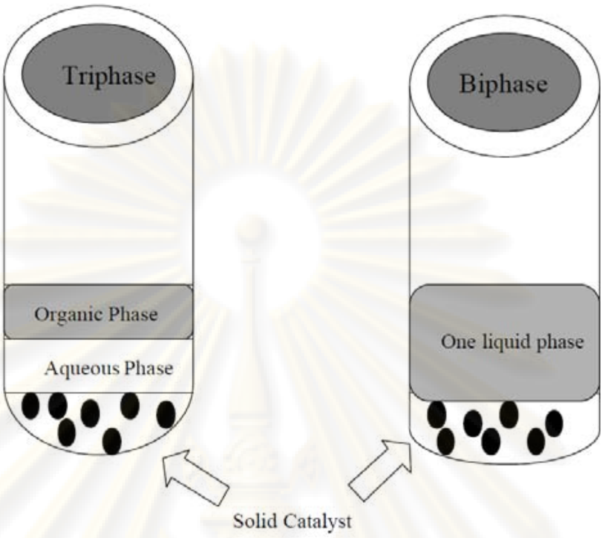


Figure 2.9 Tri-phase and bi-phase system

2.6 Literature reviewed

2.6.1 The preparation of titanium silicalite-1

Wang et al. (1999) had 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. IR spectra have a characteristic peak at about 960 cm^{-1}, which indicates that titanium has been incorporated into the framework of zeolite.

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, dut to the observation that an additional band typical for tetrahedral group $Ti(OSi)_4$ appeared in the silicalite spectrum at 960 cm^{-1}. Al MAS NMR spectrum of Al-TS-1 also showed of 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.

Li et al. (2002) had 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 differ 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.

Shenchunthichai et al. (2006) has 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 hydrogen peroxide 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 Co-TS-1 > V-TS-1 > Fe-TS-1 > Al-TS-1 > TS-1.

2.6.2 The catalytic activity of TS-1 catalysts in the hydroxylation of aromatics with H_2O_2 as an oxidant

Bhaumik et al. (1998) studied the influence of solvent conditions on benzene catalytic oxidation with H_2O_2. It had been demonstrated that using a tri-phase system (solid-liquid-liquid), in the absence of an organic co-solvent, a considerable increase in the conversion of benzene during the oxidation by the TS-1/H_2O_2 system could be achieved. Vigorous stirring was needed for the reaction to occur in the tri-phase system. Since the surface of titanium silicalite was relatively hydrophobic in nature, the benzene reactant completed more favorably with water for the diffusion and adsorption under the tri-phase conditions, resulting in higher conversion. Apart from enhancement in activity the present tri-phase method offered distinct advantages in easier product separation and thus contributed to the development of an eco-friendly process.

Kumar et al. (1999) studied the reaction of the hydroxylation of aromatics (such as benzene, toluene and anisole) under solvent-free, tri-phase conditions (solid ± liquid ± liquid), catalyzed by TS-1 using dilute H_2O_2 compared to that obtained under conventionally used bi-phase conditions in the presence of a co-solvent (solid ± liquid). The results were obtained in benzene hydroxylation under tri-phase and bi-phase conditions. In the presence of a co-solvent (bi-phase) they reported that the reaction was very slow and only catalytic activity 12 mol% of H_2O_2 efficiency could be obtained after 8 h. However, under presently used tri-phase condition, the reaction was very fast from the beginning itself reaching maximum conversion level (ca. 85 mol% H_2O_2 efficiency) in 2 h. Kinetic study showed that the selectivity for phenol also increase.

Kasemsiri et al. (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 follows the order: Fe-TS-1 (10.01%) > Al-TS-1 (5.39%) > TS-1 (1.09%) > Co-TS-1 (0.85%) > V-TS-1 (0.34%) and the selectivity of product observed follows sequence: TS-1 > Co-TS-1 > V-TS-1 > Al-TS-1 > Fe-TS-1.

CHAPTER III

EXPERIMENTAL

This chapter is divided into three major parts: (3.1) catalyst preparation, (3.2) catalyst characterization and (3.3) reaction study in hydroxylation toluene. The chemicals, apparatus and procedures for catalyst preparation are explained in section 3.1. The details of the reaction study are illustrated in section 3.2.

3.1 Catalyst preparation

3.1.1 Chemicals

All chemicals is used in this preparation procedure of Al-TS-1 catalysts are following in table 3.1.

Table 3.1 The chemicals used in the catalyst preparation and reactions

Chemical	Grade	Supplier
Toluene	Analytical	Aldrich
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
Hydrogen peroxide 30%	Analytical	Merck
Ethanol	Analytical	Merck
Aluminium(III)nitrate nonahydrate	Analytical	Fluka

3.1.2 Preparation Procedures

The preparation procedure of Al-TS-1 by rapid crystallization method is shown in figure 3.1, while the reagents used are shown in table 3.2.

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

Solution for the gel preparation			**Solution for decant-solution preparation**		
Solution A1			**Solution A2**		
$Ti[O(CH_2)_3CH_3]_4$	2.2085	g	$Ti[O(CH_2)_3CH_3]_4$	2.2085	g
TPABr	5.72	g	TPABr	7.53	g
NaCl	11.95	g	De-ionized water	60	ml
$Al(NO_3)_3{\cdot}9H_2O$	x	g	$Al(NO_3)_3{\cdot}9H_2O$	x	g
De-ionized water	60	ml	H_2SO_4 (conc.)	3.4	ml
H_2SO_4 (conc.)	3.4	ml			
Solution B1			**Solution B2**		
Sodium silicate	69	g	Sodium silicate	69	g
De-ionized water	45	ml	De-ionized water	45	ml
Solution C1			**Solution C2**		
TPABr	2.16	g	NaCl	26.27	g
NaCl	40.59	g	De-ionized water	104	ml
NaOH	2.39	g			
De-ionized water	208	ml			
H_2SO_4 (conc.)	1.55	ml			

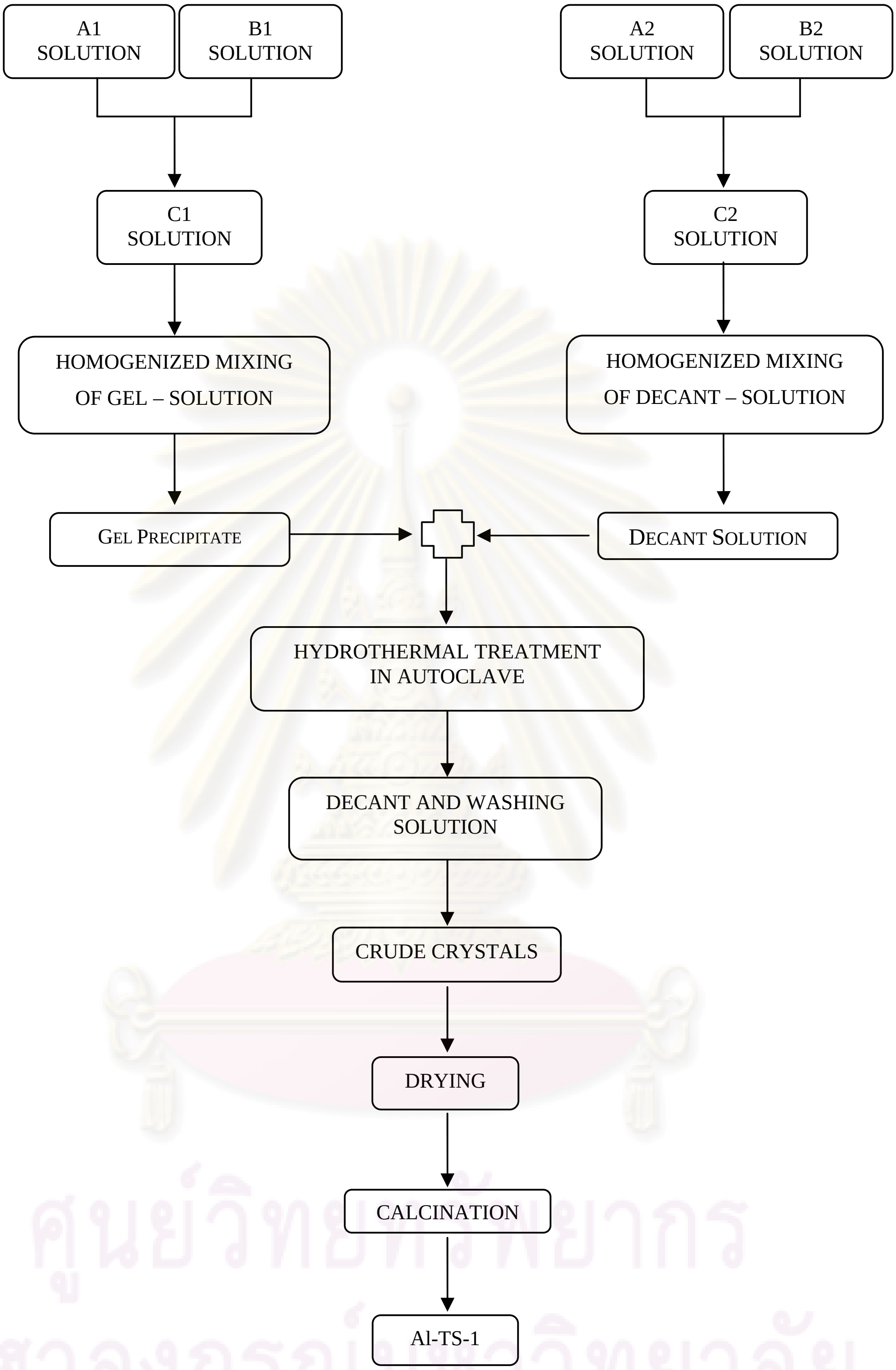


Figure 3.1 Preparation procedure of Al-TS-1 by rapid crystallization method.

In the synthesis catalyst uses titanium (IV) butoxide ($Ti[O(CH_2)_3CH_3]_4$), sodium silicate ($Na_2O\cdot SiO_2\cdot H_2O$) and aluminiumnitrate nanohydrate ($Al(N_3O)_3\cdot 9H_2O$) as the sources of cations (Ti, Si and Al respectively) for preparation of gel and decant solution. Tetrapropylammonium bromide ($(CH_3CH_2CH_2)_4NBr$) is used as the organic template. The detail procedures are as follows:

3.1.2.1 Gel solution preparation

Gel was prepared by dropping solution A1 coupling with solution B1 into solution C1, meanwhile pH value of the mixed solution was controlled in the range of 9-11 during this step. The mixed solutions were further stirred for 2 hours and then be centrifuged and switched milling to derive gel and clear liquid. This gel will be used for mixing with the decant solution in the next step.

3.1.2.2 Decant solution preparation

Decant solution was prepared by dropping solution A2 coupling with solution B2 into solution C2, meanwhile pH value of the mixed solution was controlled in the range of 9-11 during this step. The mixed solutions were further stirred for 2 hours and then centrifuged to derive gel and the clear liquid obtained is called “decant solution”.

Mixing of the prepared gel and the decant solutions leads to the derive solution for crystallization in the next step.

3.1.2.3 Crystallization

In the step of crystallization, the mixture of the solution from the previous steps is filled in a glass vessel and placed in a stainless steel autoclave. The mixture is heated from room temperature to 180°C under pressure 5 kg/cm^2 (gauge) of nitrogen gas in run time for 3 days, after that the hot mixture is cooled down to room temperature while still remains in the autoclave. The product crystals are washed with de-ionized water until the pH value of the washing water decreases from about 10 to 7. And then, the crystals are dried in an oven at 110°C for 24 hours.

3.1.2.4 Calcination

The dry crystals were calcined in an air stream at 550°C and held at that temperature for 6 h, by heating them from room temperature to 550°C with heating rate 8.6°C /min. The organic templates were burned off leaving cavities and channels in the crystals. The calcined crystals were finally cooled down to room temperature and stored in a desiccator for later use.

3.1.3 Treatment catalysts

Al-TS-1 and TS-1 were placed into a round bottom flask, and then 5M of HNO_3 aqueous solution was added. After reflux at 80°C for 3 h, the treated catalyst was 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 was performed by X-ray fluorescence (XRF) using Siemens SRS 3400 at Scientific and Technological Research Equipment Centre, Chulalongkorn University.

3.2.2 BET surface area measurement

The total surface area, pore volume and pore size were calculate using BET Micremeritrics ASAP 2020. The sample cell which contained 0.3 g of sample was placed into BET Micromeritrics ASAP 2020. After degassing step, the surface area and pore volume of catalyst were measured.

3.2.3 X-Ray Diffraction (XRD)

The crystallinity and X-ray diffraction patterns of the catalysts were 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 were carried out by using CuKα radiation with Ni filter. Scans were performed over the 2θ ranges from 6^o to 40^o.

3.2.4 Fourier transform Infrared (FT-IR)

The functional group on the catalyst surface was determined by FT-IR using Nicolet model Impact 400.

3.2.5 NH_3 Temperature Programmed Desorption (NH_3-TPD)

Temperature programmed desorption of ammonia (NH_3-TPD) was used to determine the acid properties of catalysts. The catalyst sample (0.1 g) was treated at 550°C in helium flow for 1 h and then saturated with 15%NH_3/He mixture at 80°C for 15 min. After purging with helium at 100°C for 1 h to remove weakly physisorbed NH_3, the sample was heated to 550°C at the rate 10°C/min in 50 cm^3/min of helium flow. The amount of acid sites on the catalyst surface was calculated from the desorption amount of NH_3. It was determined by measuring the areas of the desorption profiles obtained from the Micromeritics Chemisorb 2750 analyzer.

3.3 Reaction study in the hydroxylation of toluene

The hydroxylation of toluene with 30% aqueous hydrogen peroxide using TS-1 and Al-TS-1 as a catalyst is carried out in a three-necked glass flask fitted with a condenser and a magnetic stirrer as shown in figure 3.2. The reaction temperature is controlled by a constant-temperature paraffin oil bath. Typically, 1 g of TS-1 and toluene to H_2O_2 molar ratio equals to 1:1 (1.0 ml H_2O_2, 1.1 ml C_7H_8 and 50 ml of water) are used in each experiment. First, the catalyst and water, using for dispersion of the catalyst, are added into the reactor at 90°C for 1 h to drive out gases in pores of the catalyst. After that the reactor is cooled down to 70°C and toluene is added into reactor. H_2O_2 is slowly injected drop-wise using a 1 ml for 2 hr. The reaction is stopped by rapid cooling down followed by adding 50 ml of ethanol into the reactor to homogenize the aqueous phase and the organic phase. The products are analyzed by a gas chromatograph equipped with a FID detector (SHIMADZU GC9A). The conditions of the GC are listed in table 3.3.

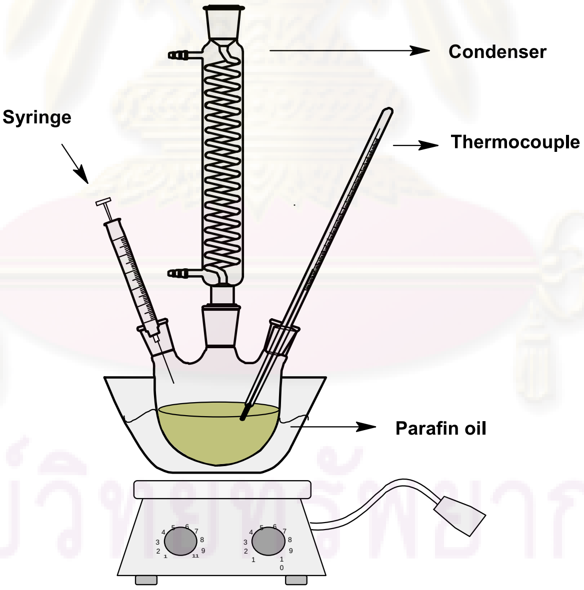


Figure 3.2 The reactor for hydroxylation of toluene.

Table 3.3 The conditions of the GC

Gas chromatograph	SHIMADZU GC9A
Detector	FID
Packed column	GP 10% SP-2100
Carrier gas	N_2 (99.999%)
Injector temperature (°C)	250
Detector temperature (°C)	250
Initial column temperature (°C)	80
Initial hold time (min)	5
Program rate (°C/min)	2
Final column temperature (°C)	230
Final hold time (min)	15
Analyzed chemicals	Toluene, Benzaldehyde and cresol

CHAPTER IV

RESULTS AND DISCUSSIONS

Chapter IV is divided into two 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), physical properties of catalysts; crystalline structure (XRD), location of titanium cation (determined from FT-IR) and surface area (measured from BET technique) are reported in section 4.1. Section 4.2 exhibits and explains the catalytic reaction of TS-1 and Al-TS-1 for the hydroxylation of toluene. The reaction results are presented in terms of conversion of hydrogen peroxide, selectivity and yield of organic products.

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.

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

Sample	% Si	% Ti	%Al	% Si/Ti
TS-1 (1day)	99.78	1.98	None	50.35
TS-1 (3 day)	98.44	2.64	None	37.29
Al-TS-1 (200)	97.47	2.80	0.20	34.77
Al-TS-1 (150)	96.64	2.97	0.22	32.57
Al-TS-1 (100)	98.78	2.30	0.28	43.02
Al-TS-1 (50)	95.19	3.66	0.48	26.03

First, let consider the effect of aging time. Data in table 4.1 show that TS-1 prepared from 1 day aging time (TS-1(1D)) has lower amount of titanium than TS-1 prepared from 3 day aging time (TS-1(3D)). This is due to longer aging time allows more stable structure to be formed. Titanium incorporated in the stable structure is not washed out in the treatment step. Therefore, all modified TS-1 catalysts are prepared using 3 day aging time.

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.

4.1.2 The crystalline structure

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).

In addition, the incorporation of aluminium into TS-1 catalyst does not affect significantly the MFI structure. After the catalysts were treated, it is found that the structures are not destroyed by the treatment with HNO_3.

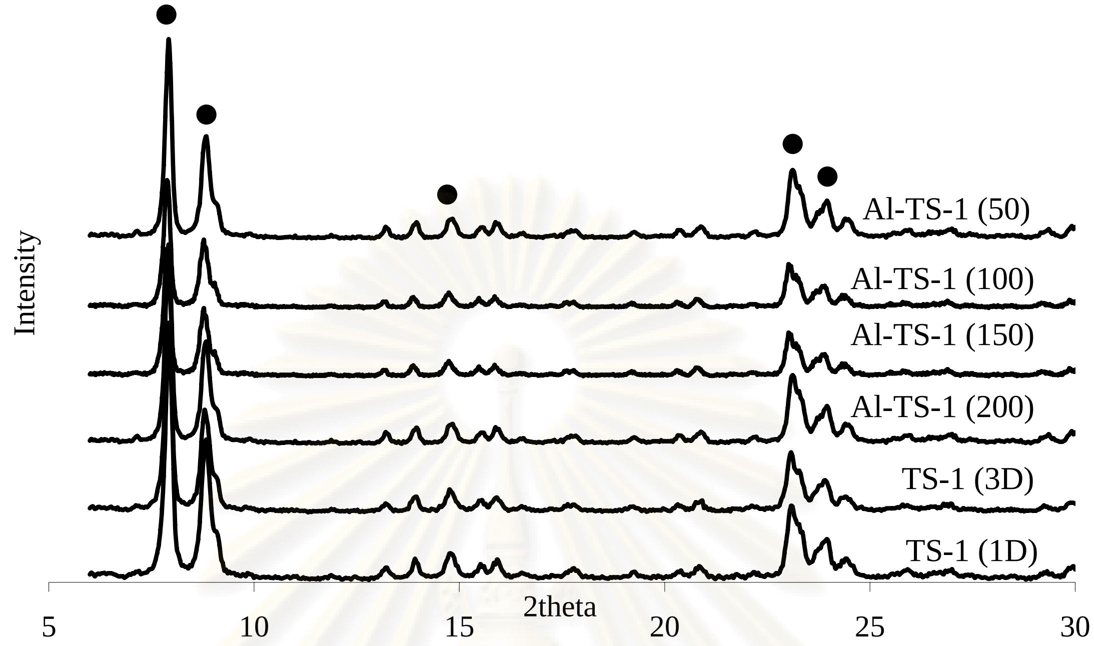


Figure 4.1 XRD patterns of TS-1 and Al-TS-1

4.1.3 Fourier-transform infrared spectroscopy (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 $Ti(SiO)_4$ which will produce an absorption band around 960 cm^{-1} (Pirutko *et al.*, 2001).

The IR absorption spectra of all samples in $Ti(SiO)_4$ absorption region is 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 $Ti(SiO)_4$ structure (Chengtian, 2002).

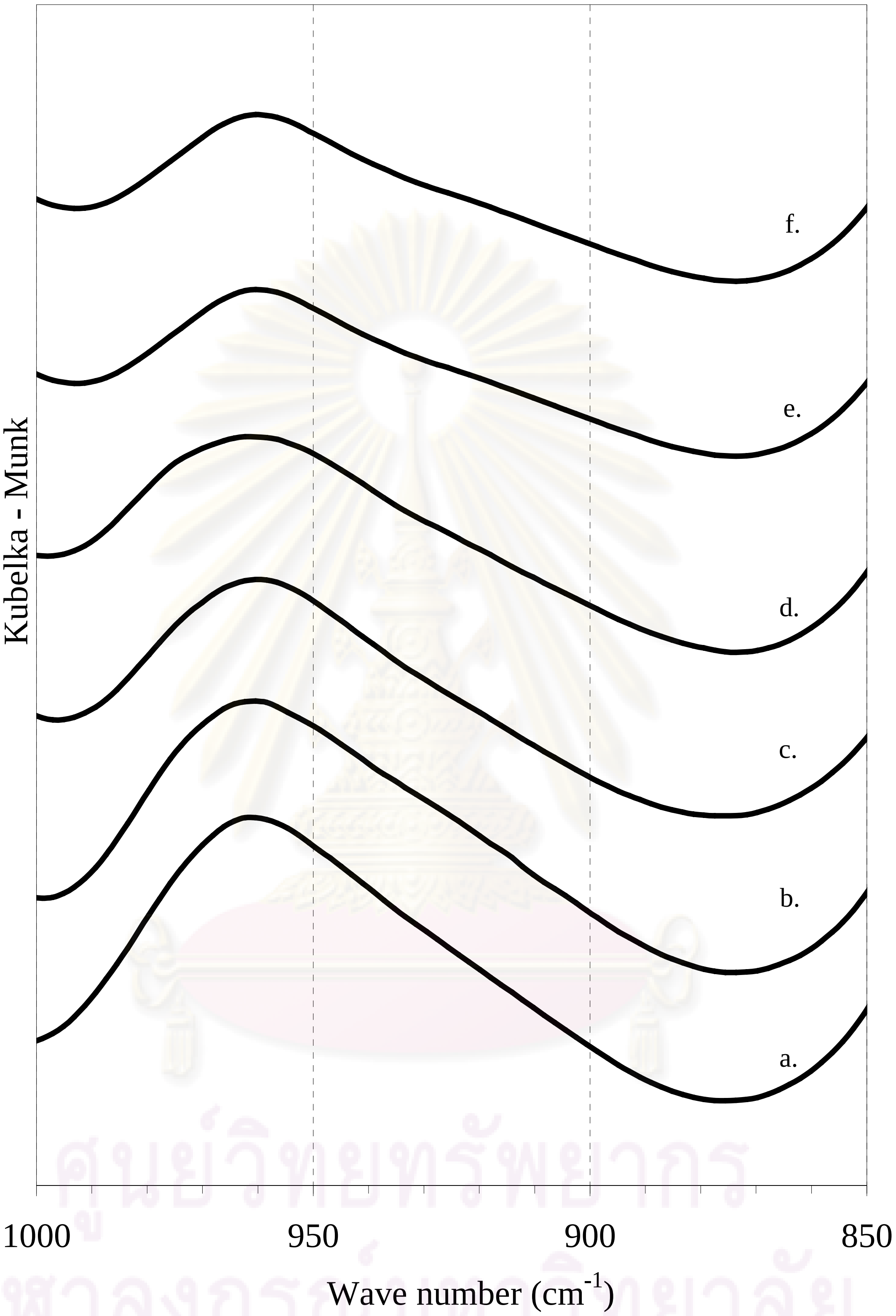


Figure 4.2 The spectra of TS-1 and Al-TS-1 (a.TS-1 b.TS-1(3day) c.Al-TS-1(200) d.Al-TS-1(150) e.Al-TS-1(100) and f.Al-TS-1(50))

Figure 4.3 illustrates the FT-IR spectra band in the range between 2000 and 4000 cm^{-1}, the absorption region of hydroxyl group. The IR spectra of all catalysts show similar broad absorption band between 2900 and 3700 cm^{-1}, representing the well-known absorption band of hydroxyl groups. Naturally, the surface of TS-1 is hydrophobic. For the hydroxylation reaction to occur, however, both hydrocarbon reactant (non-polar phase) and hydrogen peroxide (polar reactant) must exist on the catalyst surface. Any TS-1 surface, therefore, has more hydrophilicity than the other; the hydroxylation reaction will occur more easily (Chammingkwan *et al*., 2008). Since the IR spectra in figure 4.2 show that all catalyst has about the same hydrophilicity (i.e. the absorption bands have about the same size), the hydrophilicity of the surface should not be a factor that causes difference in catalytic activity of the catalysts.

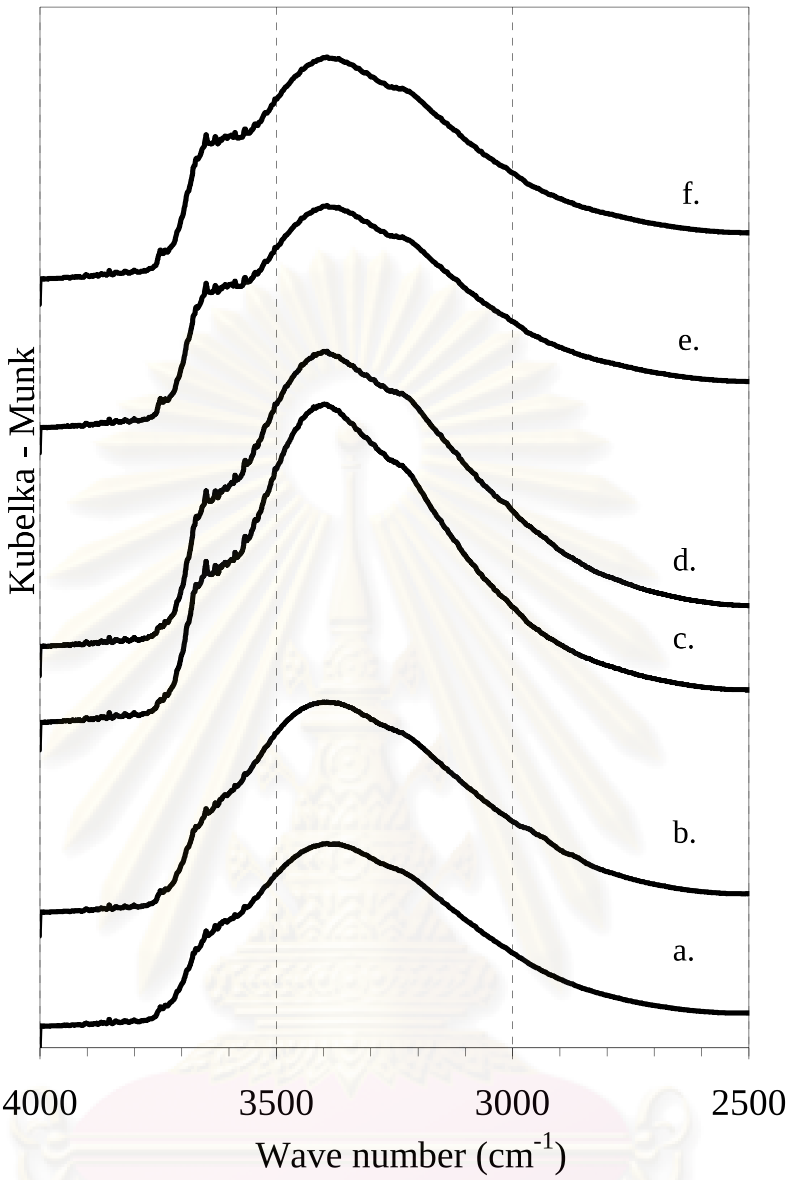


Figure 4.3 FT-IR spectra of TS-1 catalysts in wave number range between 2000 cm^{-1} and 4000cm^{-1} (a. TS-1(1day) b. TS-1(3day) c. Al-TS-1(200) d. Al-TS-1(150) e. Al-TS-1(100) and f. Al-TS-1(50))

Up to this point, a conclusion can be drawn from XRD and FT-IR analysis is that all synthesized catalysts have the MFI structure having Ti^{4+} in the framework.

4.1.4 Surface area

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 340 – 360 m^2/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

Sample	A_{BET} (m^2/g)
TS-1 (1day)	341
TS-1 (3day)	344
Al-TS-1 (50)	333
Al-TS-1 (100)	342
Al-TS-1 (150)	360
Al-TS-1 (200)	353

Since, catalyst characteristics determined from XRD, FT-IR, and BET surface area measurement are not so different, they should not affect catalytic properties of the catalyst. The major difference is the content of aluminium of each catalyst sample. The difference in catalytic activity which will be showed in the next section, therefore, should be the result of the difference in the content of aluminium of each sample.

4.2 The performance of catalytic Reaction

For a catalytic activity test of TS-1 and Al-TS-1, the hydroxylation of toluene with an aqueous hydrogen peroxide as an oxidant was performed by using a 250 ml three-necked, glass flask fitted with a condenser and a mechanical stirrer placed in a stirring block heater. This research studies the potential for the synthesis of benzaldehyde from a hydrocarbon reactant (toluene) with only a one step reaction. The experimental works are planned to cover the following effects : i) the effect of molar ratio of reactant (toluene/H_2O_2) the effect of aluminium loading, ii) the effect of temperature, and iii) the effect of aluminium loading. All conditions tested are listed in table 4.3 below. A previously study (Kasemsiri, 2008) found that this reaction gives three products which are benzaldehyde, ortho-cresol, and para-cresol. But the objective in this research is to produce benzaldehyde as the only main reaction product.

Table 4.3 Reaction conditions for TS-1 and Al-TS-1.

Catalysts	**Effect of temperature**		**Effect for molar ratio of reactant (C_7H_8/ H_2O_2)**	
TS-1 (1D)	70 °C	90 °C	1:1	2:1
TS-1 (3D)	70 °C	90 °C	1:1	2:1
Al-TS-1 (50)	70 °C	90 °C	1:1	2:1
Al-TS-1 (100)	70 °C	90 °C	1:1	2:1
Al-TS-1 (150)	70 °C	90 °C	1:1	2:1
Al-TS-1 (200)	70 °C	90 °C	1:1	2:1

Before discussing the reaction results, let have a look at the mixing phenomena occurring in the stirred reactor. In our experiment, the catalyst is submerged in the water phase. Then the reactor is heated to 90ºC and kept at this temperature for 1 hour to remove gas from the pore of the catalyst. At this moment, all catalyst pores must be filled with water. For the experiment at 70ºC the reactor is allowed to cool down to the reaction temperature. Then 1 ml of toluene is injected into the reactor followed by vigorous stirring. During this stirring period, the catalyst will contact with toluene and one or both of the following phenomena will occur:

(a) Due to the hydrophobicity of the catalyst surface, toluene may replace water on the catalyst surface and/or inside the catalyst pores up to an extended when catalyst particles contact with toluene phase during the vigorous stirring. Although water is the richest phase in the reactor, it is possible that toluene may present as the rich phase on the catalyst surface/catalyst pore, or

(b) Toluene will dissolve into the bulk water phase. Then, the dissolved toluene in the bulk water phase diffuses into the water phase filled in the pores of the catalysts particle. In this case, the concentration of toluene depends on the solubility of toluene in water.

Both phenomena are showed graphically in figure 4.4

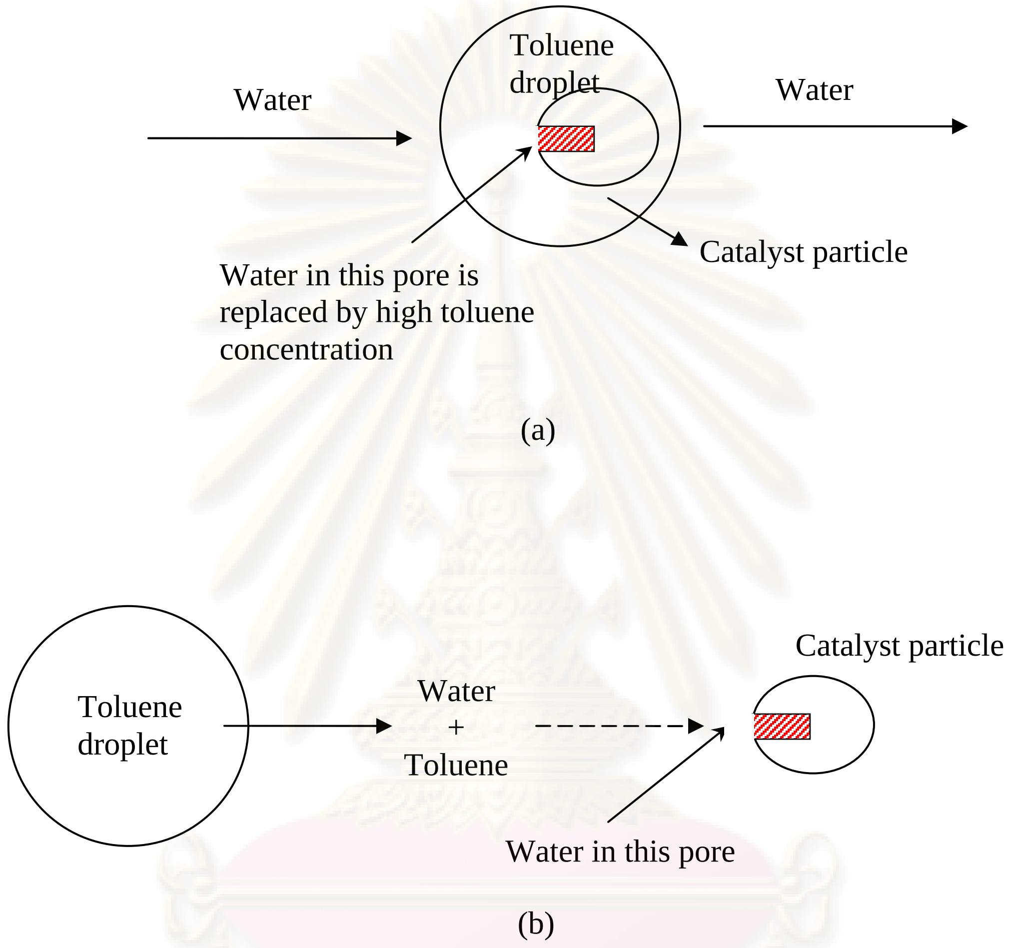


Figure 4.4 Phenomena during toluene contact with catalyst particle. (a) direct contact between catalyst particle and toluene droplet, (b) diffusion from toluene droplet through bulk water phase.

The results are related to moles of H_2O_2 because the reactant toluene can be easily separated from the tri-phase system and reused. Therefore, the considerable maximum H_2O_2 utilization is a desirable target.

It should be noted here that “one” mole of H_2O_2 is required to produce one mole of cresol while “two” of H_2O_2 is required to produce one mole of benzaldehyde.

Therefore, it is hypothesized that the molar ratio between H_2O_2 on the catalyst surface may take part in controlling which products should occur.

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

The first parameter affecting the reaction to be discussed is the molar ratio between toluene and H_2O_2. The effect of molar ratio of reactants (toluene: H_2O_2) on the conversion of H_2O_2 obtained at the reaction temperature 70°C are illustrated in figures 4.5 and 4.6. Figure 4.5 shows H_2O_2 conversion and figure 4.6 shows product selectivity. It is observed that increasing the ratio toluene: H_2O_2 from 1:1 to 2:1 results in decreasing H_2O_2 conversion.

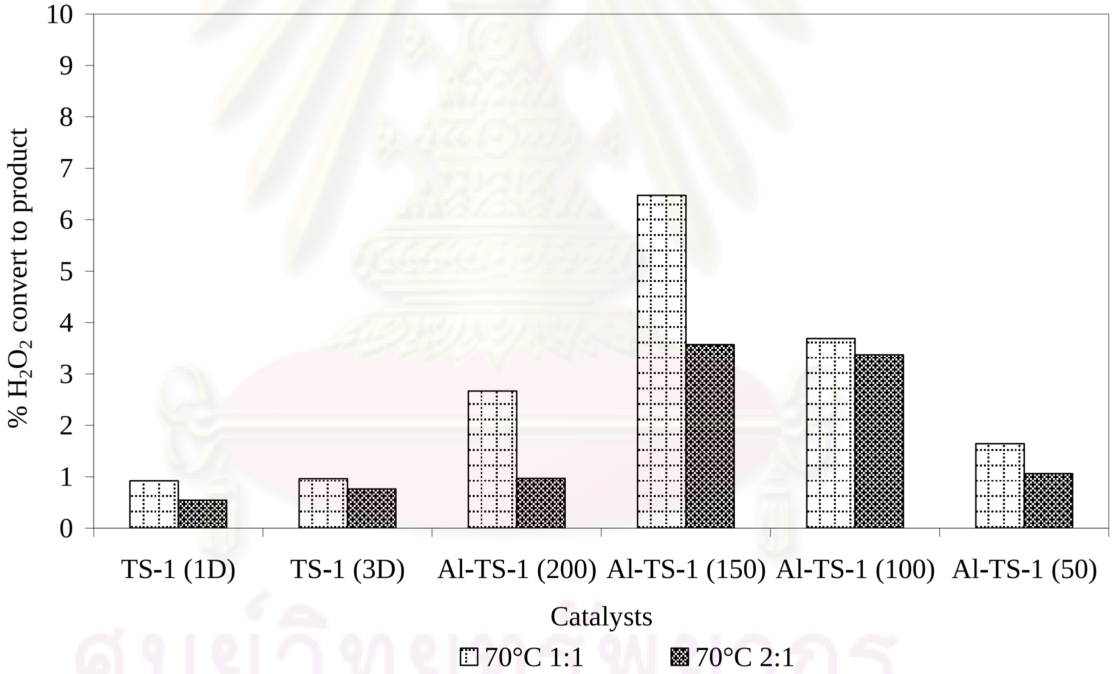


Figure 4.5 H_2O_2 conversions at reaction temperature 70°C

The observed decrease in H_2O_2 conversion of all catalysts should not be interpreted as the result of catalyst deactivation. Productivities of organic products (benzaldehyde, o-cresol, and p-cresol) of each catalyst showed in figure 4.6 illustrate the increase in cresols production when the ratio of toluene is increase. On the contrary, the productivity of benzaldehyde of all catalysts decreases. Especially, Al-

TS-1(200) and Al-TS-1(150) show a pronounce suppression of benzaldehyde formation. For example, the productivity of benzaldehyde decreases from 3.851×10^{-8} mol/sec to 2.098×10^{-8} mol/sec which is about 45% for Al-TS-1(150) and from 1.486×10^{-8} mol/sec to 5.183×10^{-9} mol/sec which is about 65% for Al-TS-1(200).

The combine productivity of cresols behaves differently from benzaldehyde when toluene: H_2O_2 ratio is increase from 1:1 to 2:1. The combine productivity of cresols slightly increases.

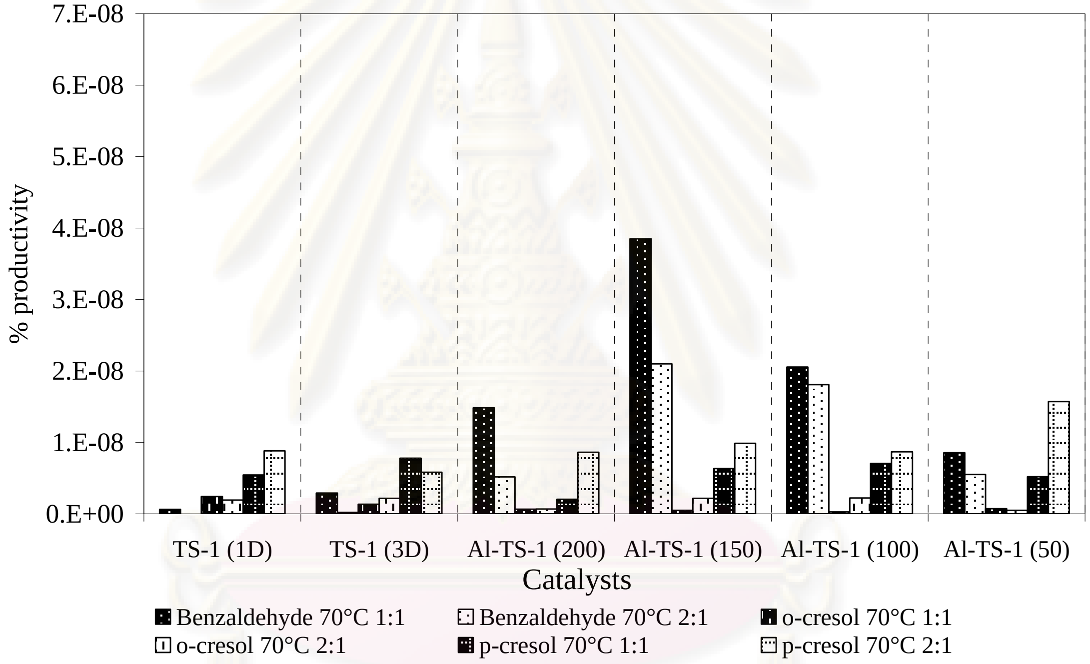


Figure 4.6 Productivity reaction temperature at 70°C

As previously mentioned in section 4.2 that the amount of H_2O_2 required for one mole of benzaldehyde is twice the amount require for one mole of cresol. Therefore benzaldehyde will be better formed on the surface having high concentration of H_2O_2. Increasing the amount of toluene, accompany with the hydrophobicity by nature of the catalyst surface, will provide less chance for H_2O_2 to exist on the catalyst surface. This is the reason why the selectivity of benzaldehyde decreases while the combine selectivity of cresols increases.

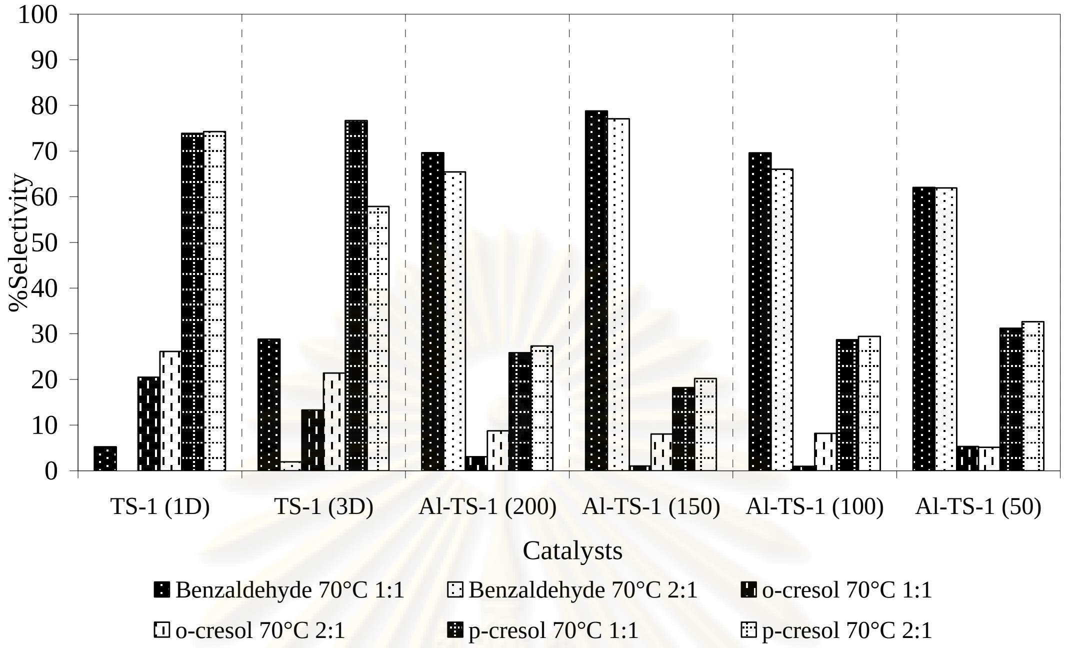


Figure 4.7 Percentage of selectivity at reaction temperature 70°C

Figures 4.8 – 4.10 exhibit H_2O_2 conversion, productivity, and selectivity respectively of the experimental results obtain from the reaction temperature 90°C. The behavior of benzaldehyde formation when toluene:H_2O_2 ratio is increased from 1:1 to 2:1 at this reaction temperature is the same as at 70°C, which can be explained by the same reason. The decreasing of H_2O_2 conversion and the significantly increase in cresol selectivity is likely the effect of the behavior of water at temperature near its boiling point. It is known that the surface tension of water decreases when the water temperature increases. Water at 90°C has lower surface tension than at 70°C thus allowing more toluene to penetrate into the catalyst pore. The surface of the catalysts is, therefore, too rich in toluene and too lean in H_2O_2. This is the reason why the decreasing of H_2O_2 conversion and the increase in cresol selectivity is observed.

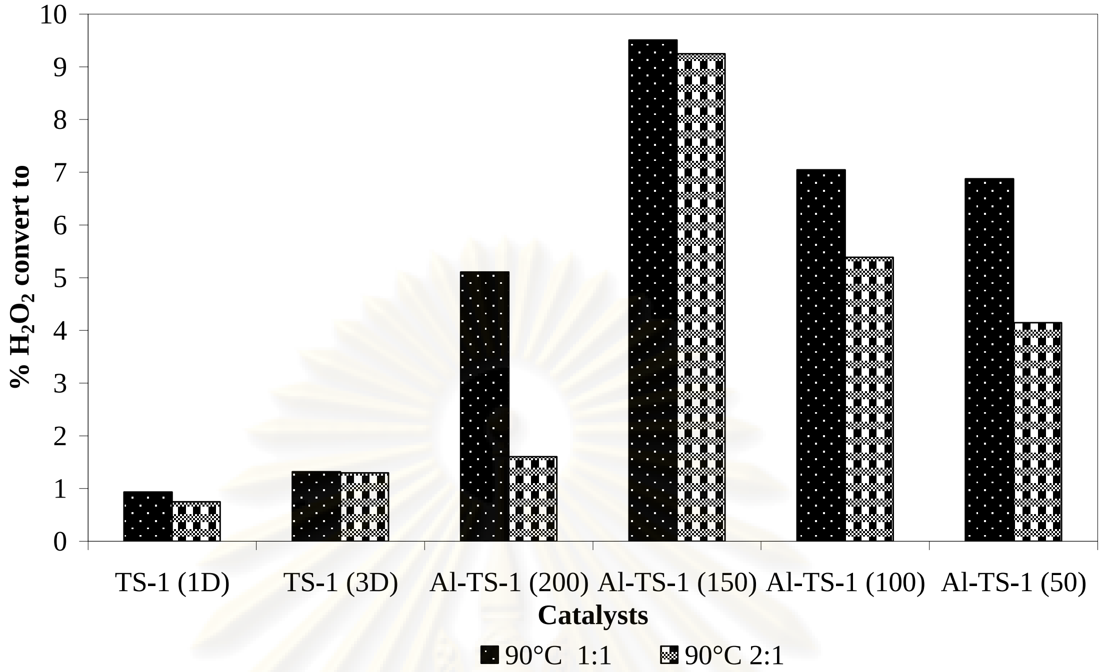


Figure 4.8 H_2O_2 convert to product at 90°C

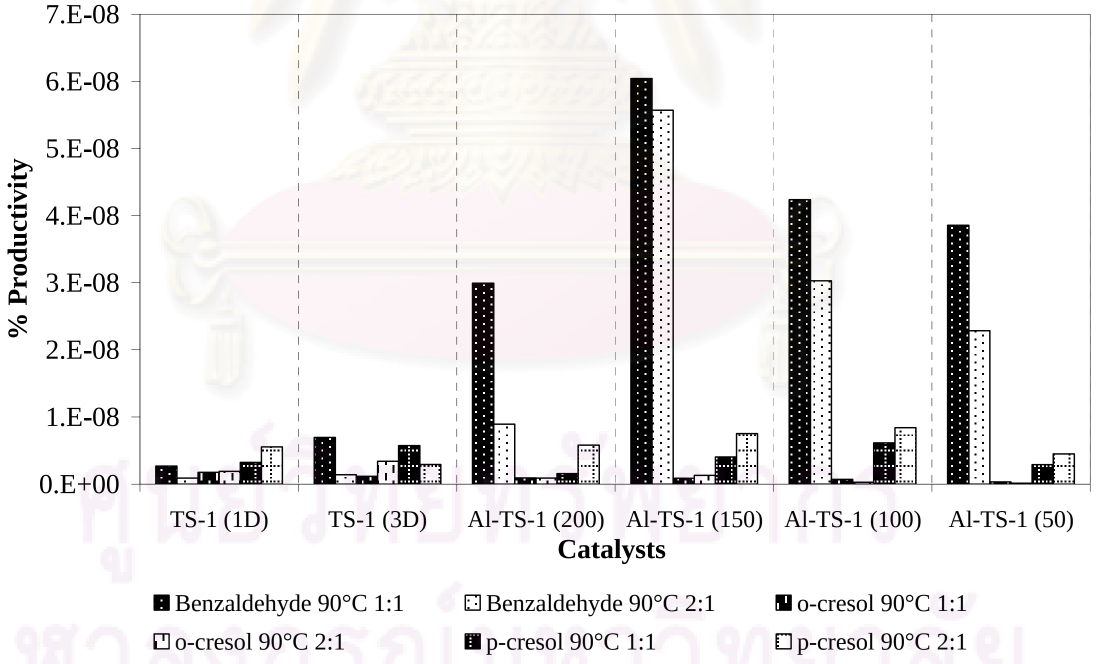


Figure 4.9 Productivity at 90°C

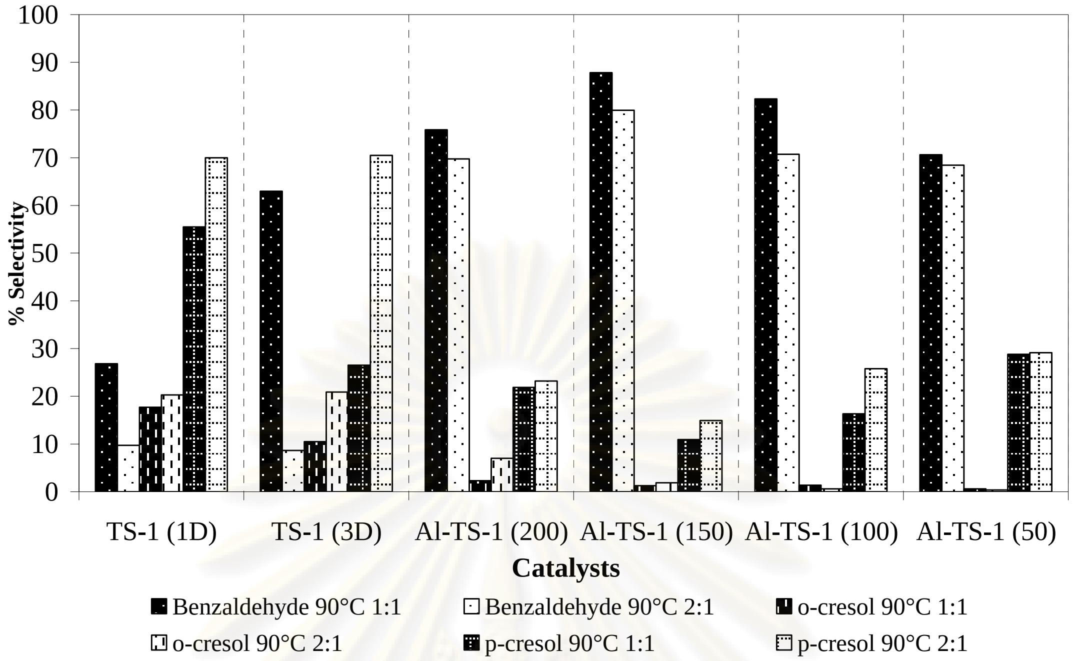


Figure 4.10 Percentage of selectivity at 90°C

4.2.2 The effect of reaction temperature

When the reaction temperature increases, the following phenomena will occur:

i) the rate constant will increase following the Arrhenius's equation
ii) the concentration of toluene in the pore of the catalyst will increase as previously above mentioned.

The hydroxylation reaction requires the existence of two reactant molecules (Toluene and H_2O_2 in our case) on the catalyst surface. At a reaction temperature, the reaction rate will depend on the ratio between the two reactant species following the Langmuir – Hinshenwood model. In our case, there are two reactions competitively occur on the catalyst surface i.e. the hydroxylation of toluene to benzaldehyde and the hydroxylation of toluene to cresol.

Phenomenon i) will increase the hydroxylation rate of toluene to benzaldehyde and cresol while phenomenon ii) will increase the selectivity to cresol as previously described in section 4.2.1. For the hydroxylation reaction of toluene to benzaldehyde both phenomena produces contradicts effects. Phenomenon i) will increase the hydroxylation rate of toluene to benzaldehyde but phenomenon ii) will decrease the selectivity to benzaldehyde due to less H_2O_2 is available on the catalyst surface.

At the same toluene to H_2O_2 ratio, it is observed that when the reaction temperature is increased from 70°C to 90°C both the productivity and selectivity of benzaldehyde increase. This result suggests that phenomenon i) plays the major role.

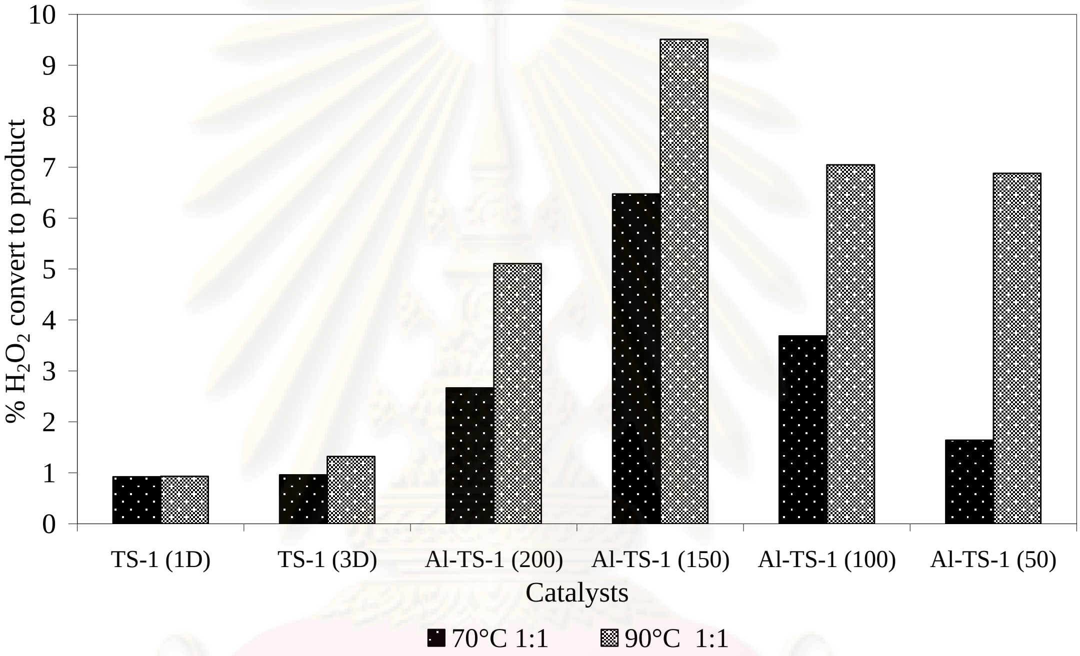


Figure 4.11 H_2O_2 convert to product with molar ratio of reactant 1:1

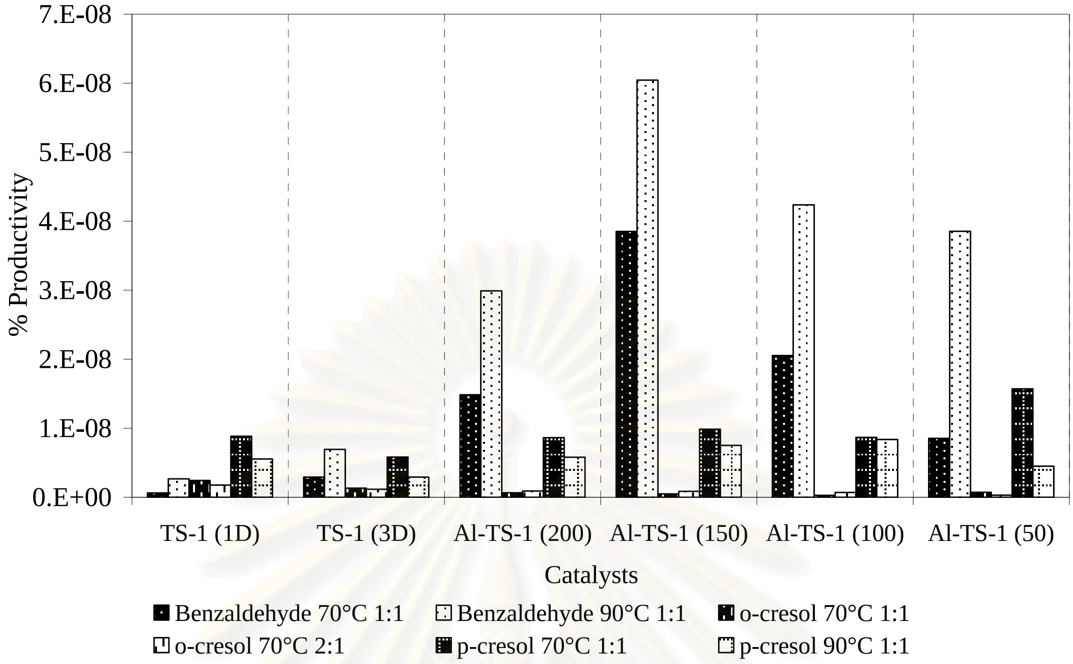


Figure 4.12 Productivity at molar ratio toluene: H_2O_2 = 1:1.

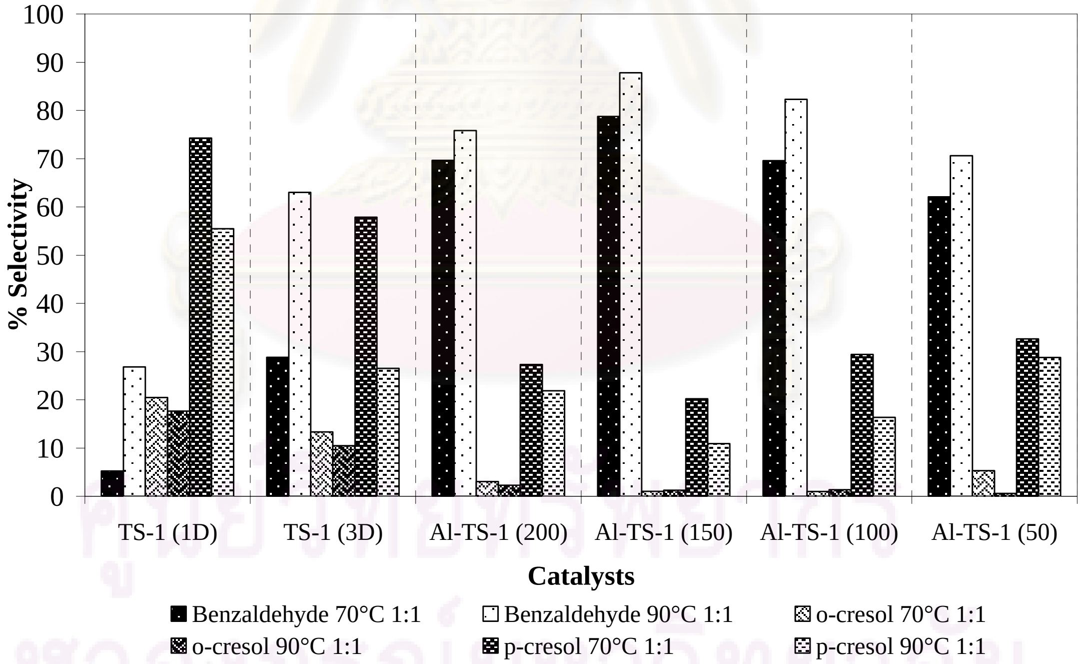


Figure 4.13 Selectivity at molar ratio of toluene: H_2O_2 = 1:1.

Consider the data obtained from using the molar ratio toluene: H_2O_2 = 2:1, the exhibited productivity and product selectivity (as showed in figures 4.14 and 4.16**)** are similar at molar ratio toluene:H_2O_2 = 1:1. When the reaction temperature is increased the productivity and selectivity of benzaldehyde increase. But as previously described in section 4.2.1 and showed in figure 4.11, when toluene:H_2O_2 ratio is increase from 1:1 to 2:1, the catalyst surface will become too rich in toluene and lack of H_2O_2 therefore, cresols are allowed to produce more.

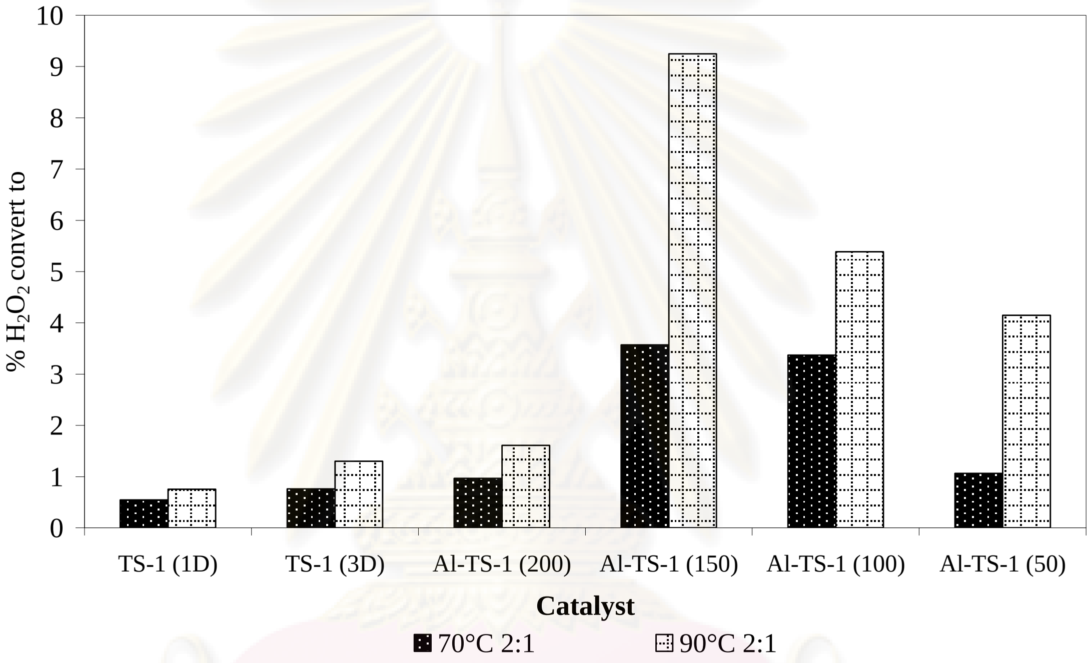


Figure 4.14 H_2O_2 convert to product with molar ratio of reactant 2:1

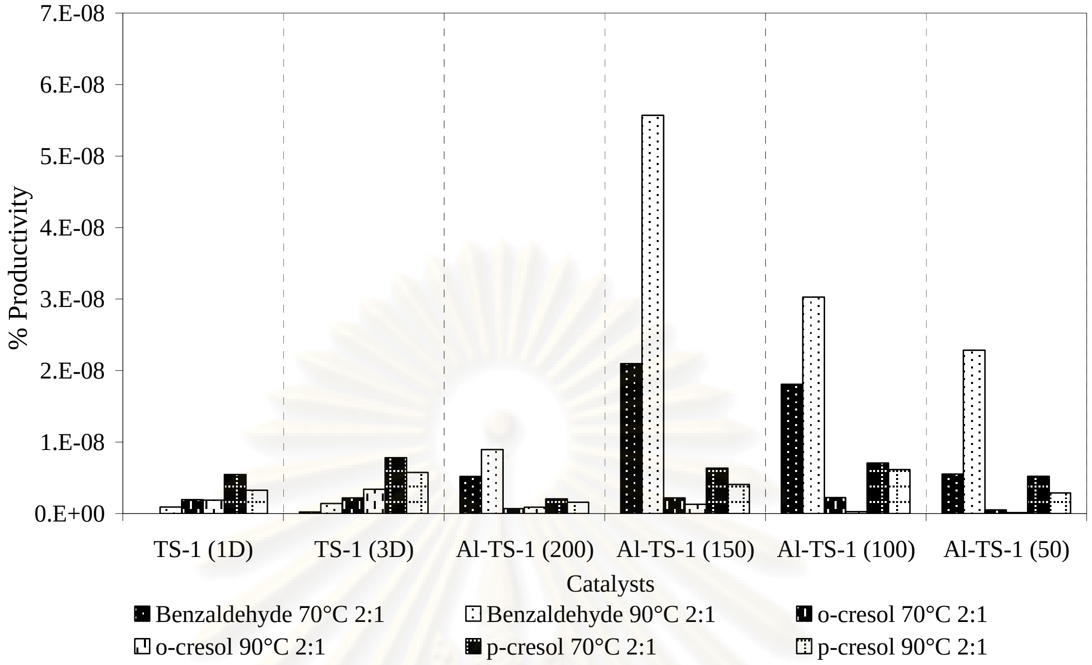


Figure 4.15 Productivity with molar ratio of toluene: H_2O_2 = 2:1

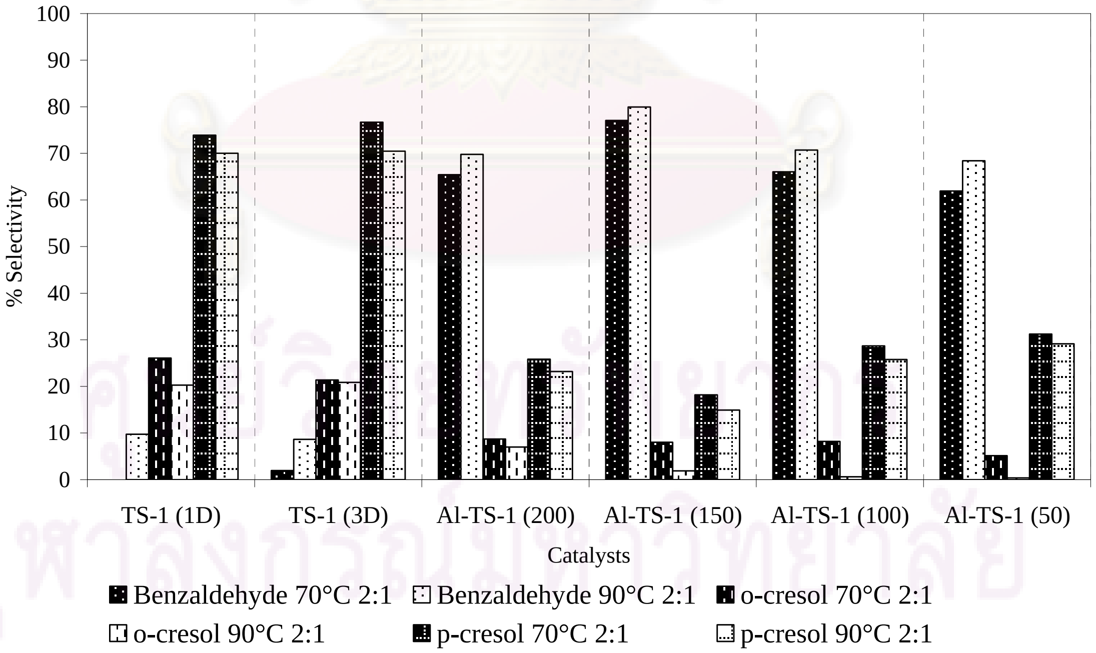


Figure 4.16 Selectivity with molar ratio toluene: H_2O_2 = 2:1

4.2.3 The importance of aluminium cation

As demonstrated in previously that the difference among the catalysts is the amount of aluminium cation. And in section 4.2 we have demonstrated that each catalyst has its own catalytic behavior. 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 NH_3-TPD measurement. The measurement results are graphically showed in figures 4.17-4.22.

The results obtained from the programme suggest that the acidic site can categorized into 3 groups, according to their desorption peaks. The first one locates around 120-150°C which will be named here “the weak acid site”. The second one locates around 150-180°C which will be named here “the medium strength acid site” and the last group locates higher than 180°C and will be named here “the strong acid site”. The location of each peak and amount of peak type of the acidic site (determined from the area under each peak are summarized in table 4.4).

Table 4.4 The strength and amount of the acid site of the catalysts

Catalyst	Total acid site	Weak acid strength		Medium acid strength		Strong acid strength	
		Temp (°C)	Site (μmol/g)	Temp (°C)	Site (μmol/g)	Temp (°C)	Site (μmol/g)
TS-1 (1D)	234	131	223	-	-	302	1
TS-1 (3D)	94	133	85	-	-	314	9
Al-TS-1 (200)	374	124	360	-	-	361	14
Al-TS-1 (150)	1689	-	-	157	1510	431	179
Al-TS-1(100)	490	-	-	134	337	360	153
Al-TS-1 (50)	442	-	-	160	329	289	113

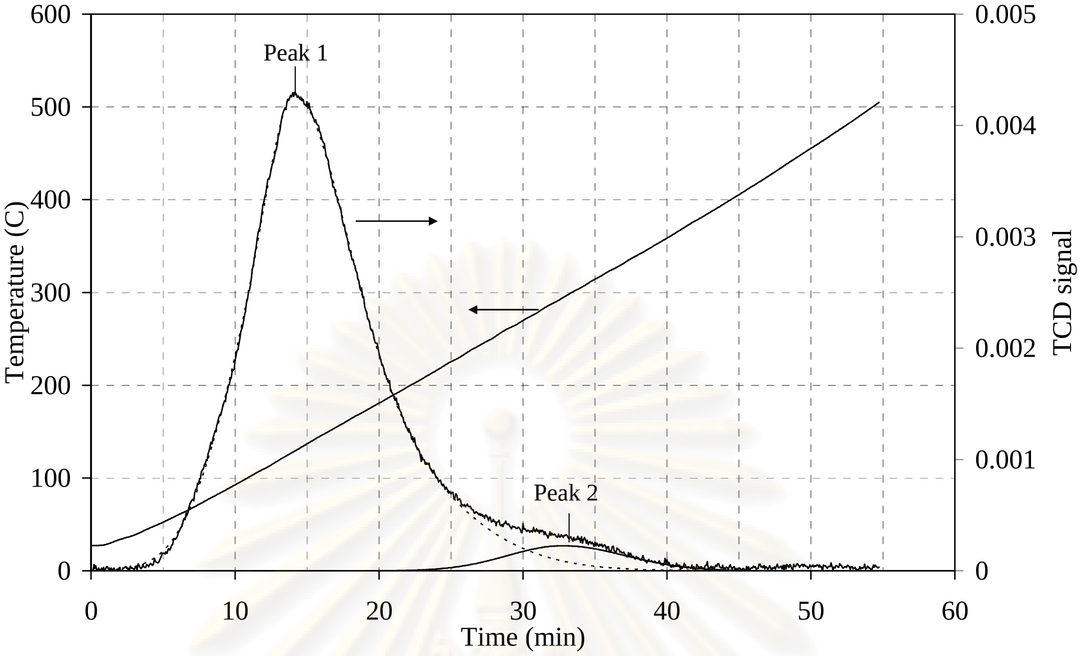


Figure 4.17 TCD signal and temperature versus time data of TS-1 (1D)

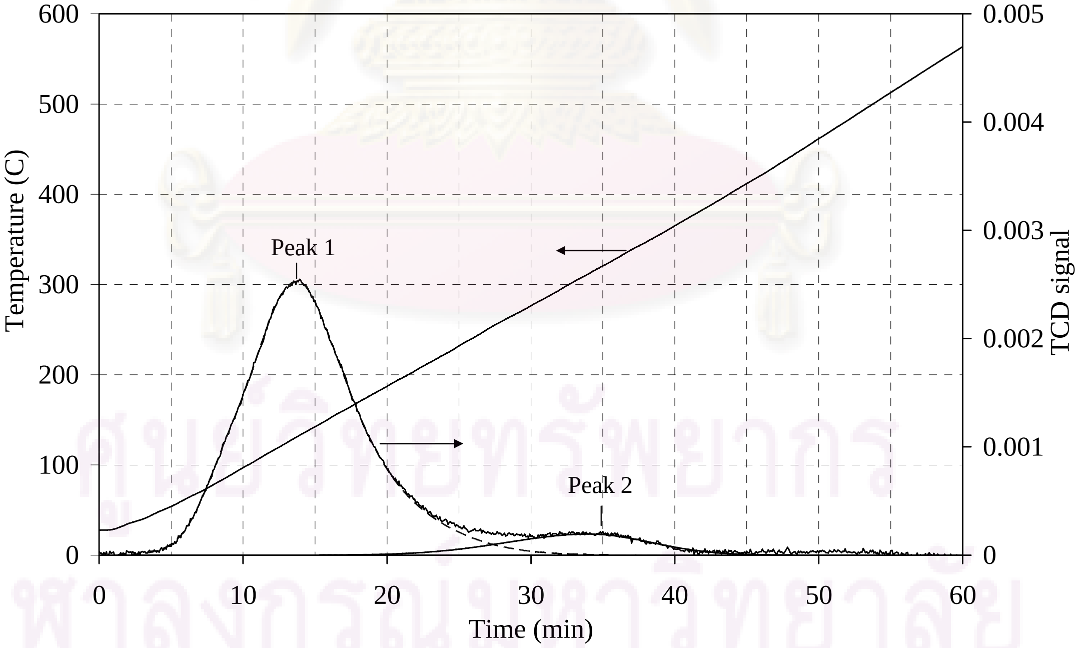


Figure 4.18 TCD signal and temperature versus time data of TS-1 (3D)

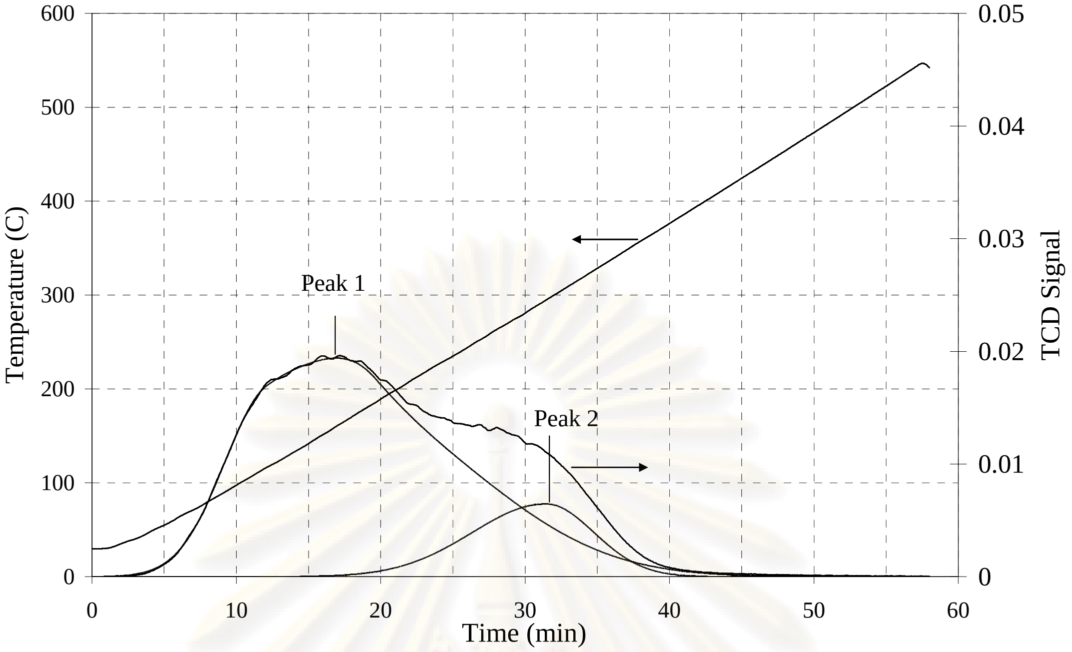


Figure 4.19 TCD signal and temperature versus time data of Al-TS-1 (50)

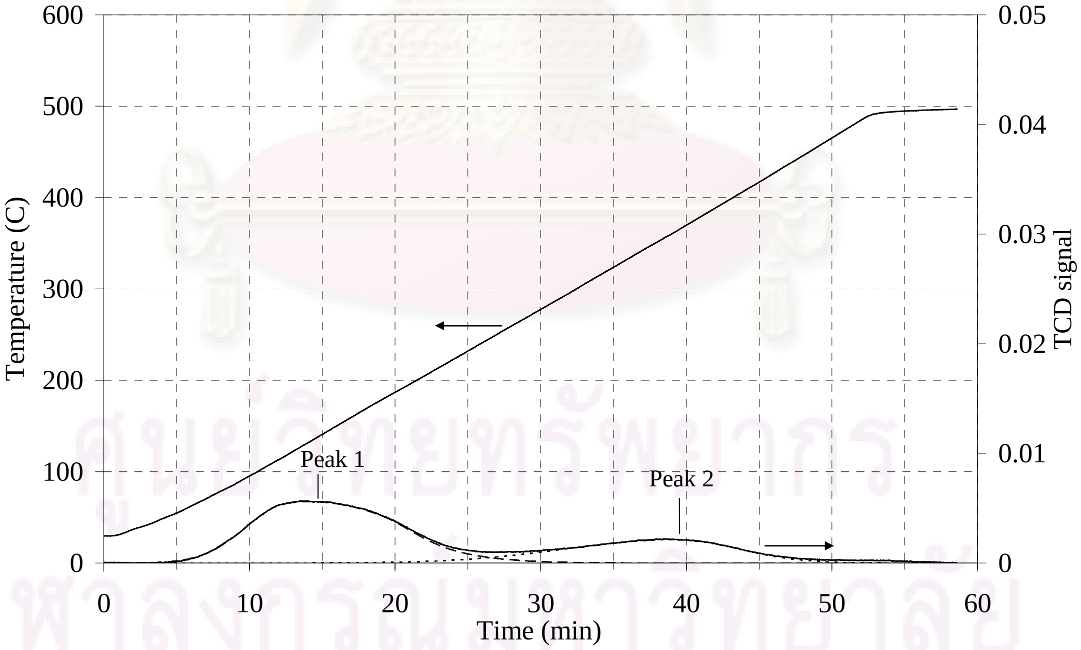


Figure 4.20 TCD signal and temperature versus time data of Al-TS-1 (100)

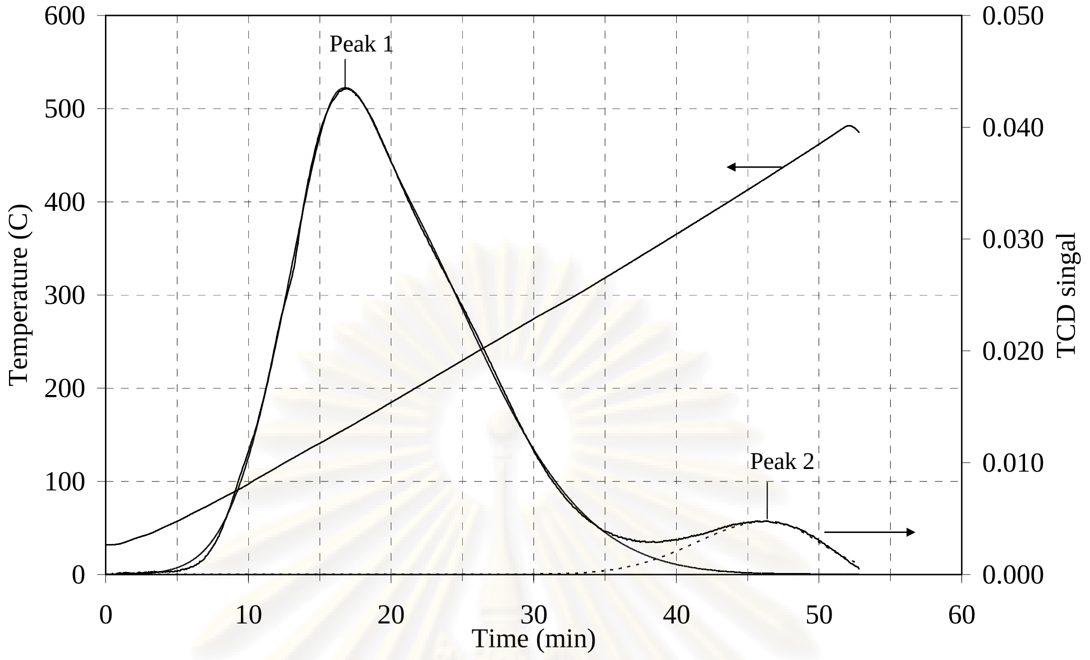


Figure 4.21 signal and temperature versus time data of Al-TS-1 (150)

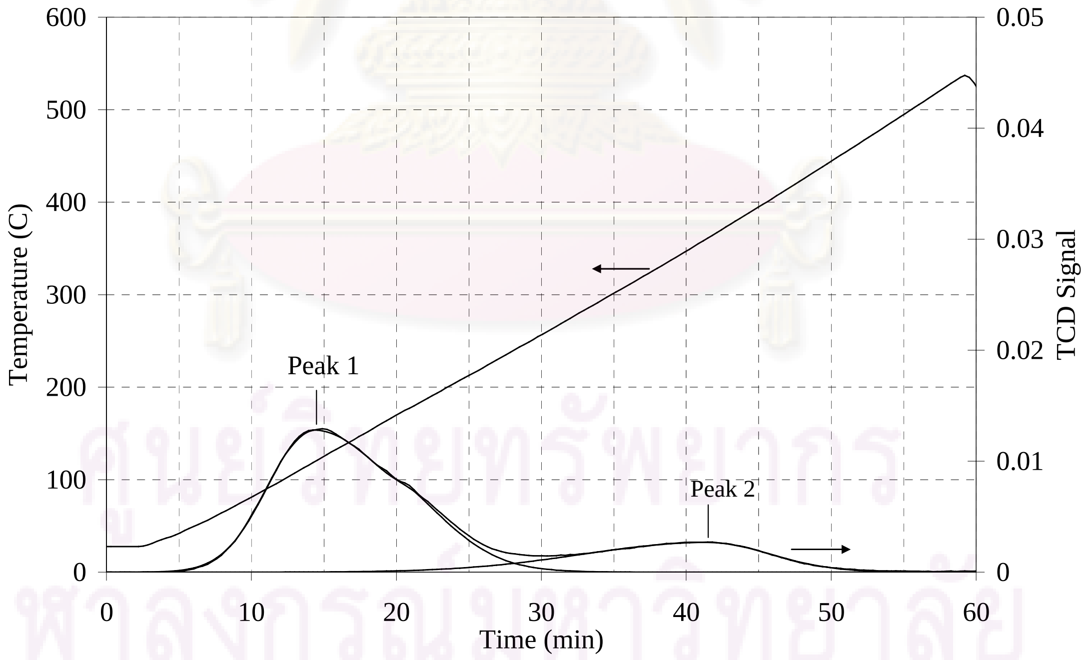


Figure 4.22 signal and temperature versus time data of Al-TS-1 (200)

The results obtained from NH_3-TPD suggest that the acidic strength of the catalysts relates to the formation of benzaldehyde. For example Al-TS-1(150) which has the strongest acidic site and highest amount of strong acid site has the highest benzaldehyde productivity and selectivity. Another example is Al-TS-1(200), which has lower amount of acidic site but stronger acidic site than Al-TS-1(50), but both catalysts can produce benzaldehyde at the same level. These results suggest that the stronger the acidic site, the more the formation of benzaldehyde.

This point indicates that the catalysts used in reactions can also give a product obtained from the side chain oxidation in case the presence of strong acid site in catalyst, the benzaldehyde selectivity tends to increase. Therefore, the temperature increasing affects to strong acid site which can promote the hydroxyl group substitution at both much benzene ring (Kasemsiri, 2007). Especially the side chain oxidation at 90°C is much more preferred than the ring substitution and the side chain oxidation at 70°C. From the results of predominant side chain oxidation reveal that all of catalysts have both mechanisms presented in figure 4.7 and their mechanisms are more influence than figure 4.6.

In summary, from all the experimental results and reasons shown above, it can be said that the formation of benzaldehyde over Al-TS-1 prefers the existence of strong acid site as well as high H_2O_2 concentration on the catalyst surface.

4.3 Proposed mechanism for the formation of benzaldehyde and cresols

It has been demonstrated above that the reaction between toluene and hydrogen peroxide 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 4.23. In this section, the mechanisms for the formation of benzaldehyde and cresols will be proposed.

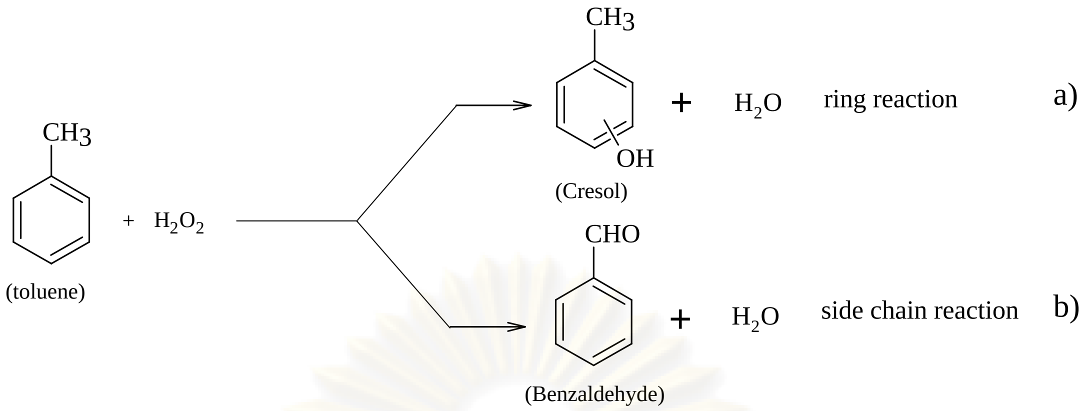


Figure 4.23 The hydroxylation of toluene at the side chain and benzene ring.

4.3.1 Proposed mechanism for the electrophilic substitution

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 (-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.

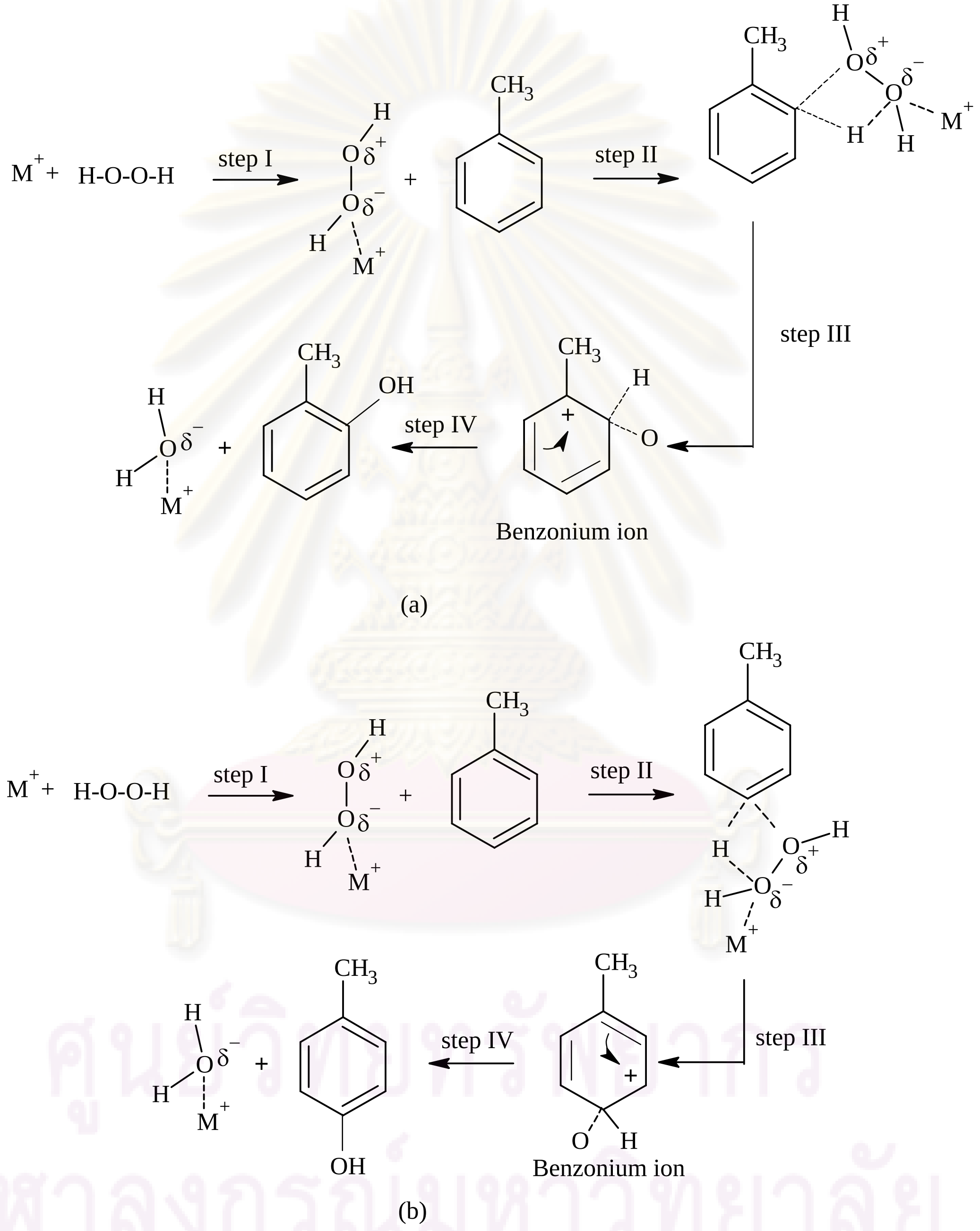
The mechanisms for the formation of o-cresol and p-cresol are showed in figure 4.24. The mechanism of cresol is proposed to consist of the following four steps:

1. The metal active site convert hydrogen peroxide 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 nucliophile, toward the electrophilic reagent.

3. The benzonium ion, in which the positive charge is delocalied by resonance to the carbon atom at ortho and para to the carbon to which the OH redical 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.



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

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

4.3.2 Proposed reaction scheme for the oxidation at the methyl group

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 replaces by free radicals (such as H-O· and H-O-O·) more easily than hydrogen atom of the ring. Such free radicals may be generated from the decomposition of hydrogen peroxide 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. The mechanism of the formation of benzaldehyde is showed in figure 4.25. The active site in figure 4.25 is possibly the cations of Al and Ti which act as acidic site having strength higher than any other catalysts.

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

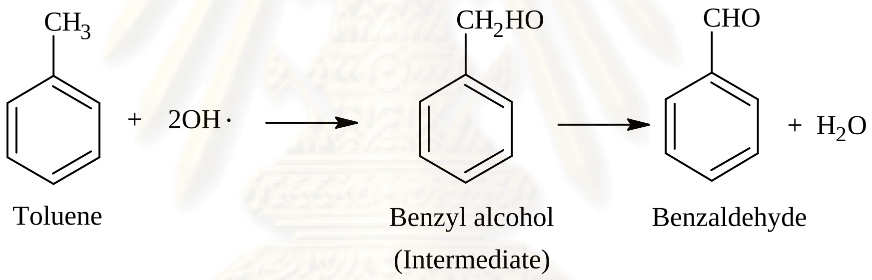


Figure 4.25 The mechanism of benzaldehyde formation**.**

4.4 Conclusions

From all of the experimental results and reasons described above, it can be concluded that Al-TS-1 has a potential to be used as a catalyst for the production of benzaldehyde via the reaction with hydrogen peroxide in a stirred reactor. The activity of the catalyst is believed to relate to the strength of the acid site of the catalyst. The stronger the acid site is the more the benzaldehyde formed. The role of aluminium is adjusting the acidity of the catalyst. The mechanism for the formation of benzaldehyde and cresols are also proposed.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

In this research, the catalytic activity of TS-1 and Al-TS-1 tested on the hydroxylation of toluene to benzaldehyde is reported. The performance of the catalysts is evaluated and the reaction mechanisms of product formation during the hydroxylation of toluene hydrogen peroxide are proposed. The experiments, results, and discussions are summarized in the first part of this chapter and the second part is recommendation for future study.

5.1 Conclusions

1. 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.

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

3. Increasing molar ratio of toluene per hydrogen peroxide from 1:1 to 2:1 to suppresses benzaldehyde formation.

4. Increasing of reaction temperature increases the reaction rate, and increases H_2O_2 conversion but will also increase cresol selectivity.

5. Strong acid site seems to play an important role in the formation of benzaldehyde. But too high acidic strength will cause severe decomposition H_2O_2.

5.2 Recommendations

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. Other acid solution for the pretreatment of TS-1 catalysts should be tried.

REFERENCES

Bhaumik, A., Mukherjee, P. and Kumar, R. (1998). Triphase Catalysis over Titanium-Silicate Molecular Sieves under Solvent-free Conditions. *J. Catal. 178*(1), 101-107.

Chengtian, W. (2002). Effects of organic solvents on the structure stability of TS-1 for the ammoximation of cyclohexanone. *React.Kinet.Catal.Lett*. 77(1), 73-81.

Chammingkwan, P. (2008). Selective oxidation of benzene over titanium-silica based catalyst. Ph. D's thesis. Chulalongkorn University.

Chammingkwan, P., Hoelderich, W.F., Mongkhonsi, T. and Kanchanawanichaku, P. (2009). Hydroxylation of benzene over TS-PQ^{TM}. catalyst. *App. Catal. A.*, 352, 1–9.

Gang, Y., Xijie, L., Jianqin, Z., Ding, M., Lijun, Z., Xianchun, L., Xiuwen, H. and Xinhe, B. (2008). Acidity and defect sites in titanium silicalite catalyst. *App.Catal. A.*, 337 58-65.

Kasemsiri P. (2007). Catalytic study of modified titanium silicalite-1 in the hydroxylation of alkyl benzene by hydrogenperoxide. *Master's Thesis*, Chulalongkorn University.

Kumar, R. and Bhaumik, A. (1998). Triphase, solvent-free catalysis over the TS-1/H_2O_2 system in selective oxidation reactions. *Microporous and Mesoporous Materials. 21*(4-6), 497-504.

Kumar, R., Mukherjee, P., and Bhaumik, A. (1999). Enhancement in the reaction rates in the hydroxylation of aromatics over TS-1/H_2O_2 under solvent-free triphase conditions. *Catalysis Today*. 49(1-3), 185-191.

Li, G., Lee, M. and Porter, F. (2002). The synthesis and characterization of titanium silicalite-1. *J. Mater. Sci.* 37, 1959 – 1965.

Mantegazza M.A. (1999). Selecitive oxidations with hydrogen peroxide and titanium silicalite catalyst, *J. Molecular Catalysis A: Chemical*, 146, 223-228.

Mukherjee P. (2000). *Solvent-free, triphase catalytic oxidation reactions over TS-1/H_2O_2 system*. PhD Thesis, Catalysis division national chemical laboratory.

Ovejero, G., Van, R., Grieken, M., Uguina, D. and Serrano, P. (1998). Study on the Ti and Al coincorporation into the MFI zeolitic structure. *J. Mater. Chem.* 2269-2276.

Pirutko, L. V., Uriate, A. K., Chernyavsky, V. S. and Kharitonov, A. S. (2001). Preparation and catalytic study of metal modified TS-1 in the oxidation of benzene to phenol by N_2O. *Micro. Meso. Mater.* 48, 345-353.

Robert, C., Atkins, F. and Carey, A. (1944). *Oraganic chemistry: a brief course 3rd ed*., McGraw-Hill, New York, 147-206.

Shenchunthichai. (2004). *Catalytic study of iron, aluminium, cobalt and vanadium modified titanium silicalites-1 in the hydroxylation of benzene to phenol by hydrogen peroxide*, Master's Thesis, Chulalongkorn University.

Sheng, X., Guo, X. and Li, G. (2002). Synthesis of titanium silicalite (TS-1) from the TPABr system and its catalytic properties for epoxidation of propylene. *J. Catal.* 74, 65–75.

Tosheva L. (1999). *Zeolite Macrostructures*, Licentiate thesis.

Wang, X. and Xin-wen, G. (1999). Synthesis, characterization and catalytic properties of low cost titanium silicalite, *J. Catal. Today.* 51, 177-186.

Zhao, Q., Bao, X. H., Han, X.W., Liu, X.M., Tan, D.L., Lin, L.W., Guo, X.W., Li, G. and Wang, X.S. (2000). Studies on the crystallization process of titanium silicalite-1 (TS-1) synthesized using tetrapropylammonium bromine as a template. *Material Chemistry and Physics.* 66, 41-50.

APPENDICES

APPENDIX A

ZEOLITES

Zeolites are the aluminosilicate members of the family of microporous solids known as "molecular sieves". The term molecular sieve refers to a particular property of these materials, i.e. the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the diameters of the tunnels. These are conventionally defined by the ring size of the aperture, where, for example, the term "8 rings" refers to a closed loop that is built from 8 tetrahedral coordinated silicon (or aluminium) atoms and 8 oxygen atoms. These rings are not always perfectly flat and symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pore openings for all rings of one size are not identical. Zeolite with 10-membered oxygen rings normally possesses a high siliceous framework structure. They are of special interest in industrial applications. In fact, they were the first family of zeolite that was synthesized with organic ammonium salts. With pore openings close to the dimensions of many organic molecules, they are particularly useful in shape selective catalysis. The 10-membered oxygen ring zeolites also possess other important characteristic properties including high activity, high tolerance to coking and high hydrothermal stability.

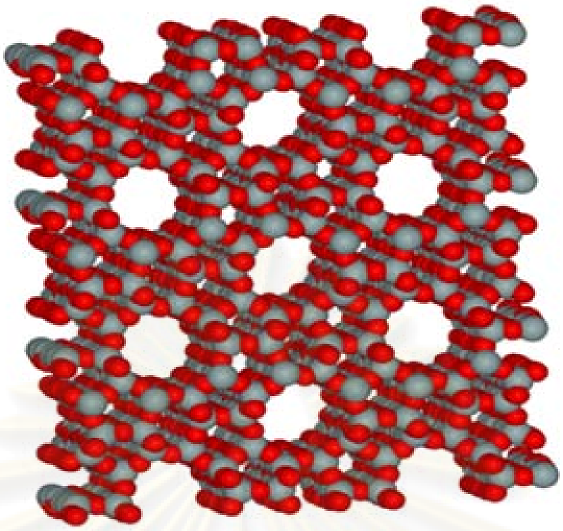


Figure A1 The micro porous molecular structure of a zeolite, ZSM-5. (en.wikipedia.org/wiki/Zeolite)

Shape selectivity

Many reactions involving carbonium intermediates are catalyzed by acidic zeolite. With respects to a chemical standpoint the reaction mechanisms are nor fundamentally different with zeolites or with any the acidic oxides. The shape selective characteristics of zeolites influence their catalytic phenomena by three modes: shape selectivity, reactants shape selectivity, products shape selectivity and transition states shape selectivity (Figure A2).

Reactants of charge selectivity results from the limited diffusion of some of the reactants, which cannot effectively enter and diffuse inside crystal pore structures of the zeolites. Product shape selectivity occurs as slowly diffusing product molecules cannot escape from the crystal and undergo secondary reaction. This reaction path is established by monitoring changes in product distribution as a function of varying contact time.

Restricted transition state shape selectivity is a kinetic effect from local environment around the active site, the rate constant for a certain reaction mechanism is reduced of the space required for formation of necessary transition state is restricted.

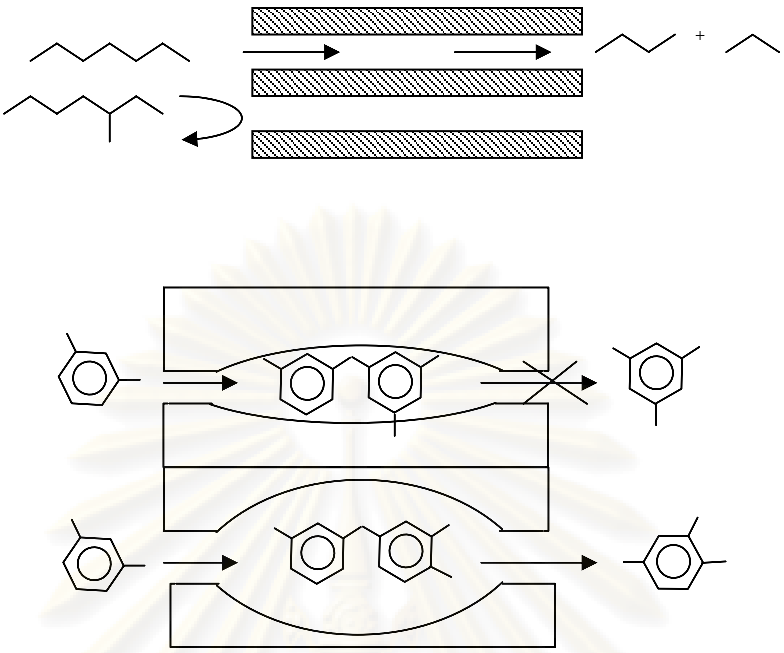


Figure A2 Diagram of shape selectivity on zeolite.

The critical diameter (as opposed to the length) of the molecules and the pore channel diameter of zeolites are important in predicting shape selective effects. However, molecules are deformable and can pass through opening, which are smaller than their critical diameters. Hence, not only size but also the dynamics and structure of the molecules must be taken into account.

Acidity

Acidity in zeolites increases with decreasing Si:Al ratio, since acid sites are associated with Al ions; acidity is also a function of cation. H-sieves are strong acids but often too unstable for commercial use. Nevertheless, zeolites exchanged with di- and trivalent ions are sufficiently acidic; for example, Ca^{2+} is thought to be present as $Ca(OH)^{+}$ plus H^{+}. ALPOs are mildly acidic relative to the aluminosilicates. The Bronsted and Lewis acidities of zeolites play important roles in their abilities to catalyze various hydrocarbon reactions, e.g. cracking and isomerization.

APPENDIX B

DATA OF EXPERIMENTS

1. Data for the effect of molar ratio of reactant (toluene: H_2O_2) in section 4.2.1

Table B1 Data of the percentage of H_2O_2 convert to product at 70°C for figure 4.5, Page 34

Catalyst	70°C 1:1	70°C 2:1
TS-1 (1D)	0.92	0.55
TS-1 (3D)	0.96	0.76
Al-TS-1 (200)	2.67	0.97
Al-TS-1 (150)	6.47	3.57
Al-TS-1 (100)	3.69	3.37
Al-TS-1 (50)	1.64	1.06

Table B2 Data of percentage of productivity 70°C for figure 4.6, Page 35

Catalyst	**70°C 1:1**			**70°C 2:1**		
	Benzaldehyde	**o-cresol**	**p-cresol**	**Benzaldehyde**	**o-cresol**	**p-cresol**
TS-1 (1D)	6.24E-10	2.44E-09	5.47E-09	0	1.93E-09	8.84E-09
TS-1 (3D)	2.91E-09	1.35E-09	5.85E-09	1.99E-10	2.17E-09	7.78E-09
Al-TS-1 (200)	1.49E-08	6.51E-10	2.05E-09	5.18E-09	6.92E-10	8.63E-09
Al-TS-1 (150)	3.85E-08	4.99E-10	6.34E-09	2.1E-08	2.18E-09	9.88E-09
Al-TS-1 (100)	2.06E-08	2.85E-10	7.07E-09	1.81E-08	2.24E-09	8.69E-09
Al-TS-1 (50)	8.54E-09	7.33E-10	5.21E-09	5.51E-09	5.06E-10	1.57E-08

Table B3 Data of percentage of selectivity 70°C for figure 4.7, Page 36

Catalyst	**70°C 1:1**			**70°C 2:1**		
	Benzaldehyde	**o-cresol**	**p-cresol**	**Benzaldehyde**	**o-cresol**	**p-cresol**
TS-1 (1D)	5.24	24.76	70.00	0.00	26.10	73.9
TS-1 (3D)	28.82	13.33	57.85	2.42	20.92	76.66
Al-TS-1 (200)	71.64	4.14	24.22	63.96	6.73	29.31

Catalyst	70°C 1:1			70°C 2:1		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
Al-TS-1 (150)	80.77	1.32	17.91	70.88	8.31	20.81
Al-TS-1 (100)	71.61	1.60	26.79	62.41	8.17	29.42
Al-TS-1 (50)	65.05	5.33	29.62	61.92	5.12	32.96

Table B4 Data of the percentage of H_2O_2 convert to product at 90°C for figure 4.8, Page 37

Catalysts	90°C 1:1	90°C 2:1
TS-1 (1D)	0.93	0.75
TS-1 (3D)	1.32	1.30
Al-TS-1 (200)	5.11	1.61
Al-TS-1 (150)	9.51	9.25
Al-TS-1 (100)	7.05	5.39
Al-TS-1 (50)	6.88	4.15

Table B5 Data of productivity at 90°C for figure 4.9, Page 37

Productivity						
Catalyst	**90°C 1:1**			**90°C 2:1**		
	Benzaldehyde	**o-cresol**	**p-cresol**	**Benzaldehyde**	**o-cresol**	**p-cresol**
TS-1 (1D)	2.69E-09	1.77E-09	3.25E-09	9.05E-10	1.89E-09	5.55E-09
TS-1 (3D)	6.94E-09	1.16E-09	5.73E-09	1.41E-09	3.4E-09	2.92E-09
Al-TS-1 (200)	2.99E-08	9.1E-10	1.58E-09	8.93E-09	8.98E-10	5.82E-09
Al-TS-1 (150)	6.04E-08	8.57E-10	4.05E-09	5.57E-08	1.3E-09	7.52E-09
Al-TS-1 (100)	4.24E-08	7.02E-10	6.14E-09	3.03E-08	2.6E-10	8.41E-09
Al-TS-1 (50)	3.86E-08	3.23E-10	2.88E-09	2.28E-08	1.23E-10	4.49E-09

Table B6 Data of selectivity at 90C for figure 4.10, Page 38

Selectivity						
Catalyst	**90°C 1:1**			**90°C 2:1**		
	Benzaldehyde	**o-cresol**	**p-cresol**	**Benzaldehyde**	**o-cresol**	**p-cresol**
TS-1 (1D)	26.84	17.67	55.49	8.72	19.28	72.00
TS-1 (3D)	63.00	10.48	26.52	8.64	20.87	70.49
Al-TS-1 (200)	75.83	2.31	21.86	69.13	6.02	24.85
Al-TS-1 (150)	87.83	1.24	10.93	79.94	1.87	18.19
Al-TS-1 (100)	82.30	1.37	16.33	70.71	0.61	28.68
Al-TS-1 (50)	70.63	0.59	28.78	68.42	0.37	31.21

2. Data for the effect of temperature in chapter 4.2.1

Table B7 Data of the percentage of H_2O_2 convert to product with molar ratio of toluene: H_2O_2 as 1:1 for figure 4.11, Page 39

Catalyst	70°C 1:1	90°C 1:1
TS-1 (1D)	0.92	0.93
TS-1 (3D)	0.96	1.32
Al-TS-1 (200)	2.67	5.11
Al-TS-1 (150)	6.47	9.51
Al-TS-1 (100)	3.69	7.05
Al-TS-1 (50)	1.64	6.88

Table B8 Data of the percentage of productivity with molar ratio of toluene: H_2O_2 as 1:1 for figure 4.12, Page 40

Productivity						
Catalyst	70°C 1:1			90°C 1:1		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
TS-1 (1D)	6.24E-10	2.44E-09	5.47E-09	2.69E-09	1.77E-09	3.25E-09

Productivity						
Catalyst	70°C 1:1			90°C 1:1		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
TS-1 (3D)	2.91E-09	1.35E-09	5.85E-09	6.94E-09	1.16E-09	5.73E-09
Al-TS-1 (200)	1.49E-08	6.51E-10	2.05E-09	2.99E-08	9.1E-10	1.58E-09
Al-TS-1 (150)	3.85E-08	4.99E-10	6.34E-09	6.04E-08	8.57E-10	4.06E-09
Al-TS-1 (100)	2.06E-08	2.85E-10	7.07E-09	4.24E-08	7.02E-10	6.14E-09
Al-TS-1 (50)	8.54E-09	7.33E-10	5.21E-09	3.86E-08	3.23E-10	2.88E-09

Table B9 Data of percentage of selectivity with molar ratio of toluene: H_2O_2 as 1:1 for figure 4.13, Page 40

Selectivity						
Catalyst	70°C 1:1			90°C 1:1		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
TS-1 (1D)	5.24	24.76	70.00	26.84	17.67	55.49
TS-1 (3D)	28.82	13.33	57.85	63.00	10.48	26.52

Selectivity						
Catalyst	**70°C 1:1**			**90°C 1:1**		
	Benzaldehyde	**o-cresol**	**p-cresol**	**Benzaldehyde**	**o-cresol**	**p-cresol**
Al-TS-1 (200)	71.64	4.14	24.22	75.83	2.31	21.86
Al-TS-1 (150)	80.77	1.32	17.91	87.83	1.24	10.93
Al-TS-1 (100)	71.61	1.60	26.79	82.30	1.37	16.33
Al-TS-1 (50)	65.05	5.33	29.62	70.63	0.59	28.78

Table B10 Data of the percentage of H_2O_2 convert to product with molar ratio of toluene: H_2O_2 as 2:1 for figure 4.14, Page 41

Catalyst	70°C 2:1	90°C 2:1
TS-1 (1D)	0.55	0.75
TS-1 (3D)	0.76	1.30
Al-TS-1 (200)	0.97	1.61
Al-TS-1 (150)	3.57	9.25
Al-TS-1 (100)	3.37	5.39
Al-TS-1 (50)	1.06	4.15

Table B11 Data of the percentage of productivity with molar ratio of toluene: H_2O_2 as 2:1 for figure 4.15, Page 42

Productivity						
Catalyst	**70°C 2:1**			**90°C 2:1**		
	Benzaldehyde	**o-cresol**	**p-cresol**	**Benzaldehyde**	**o-cresol**	**p-cresol**
TS-1 (1D)	0	1.93E-09	8.84E-09	9.05E-10	1.89E-09	5.55E-09
TS-1 (3D)	1.99E-10	2.17E-09	7.78E-09	1.41E-09	3.4E-09	2.92E-09
Al-TS-1 (200)	5.18E-09	6.92E-10	8.63E-09	8.93E-09	8.98E-10	5.82E-09
Al-TS-1 (150)	2.1E-08	2.18E-09	9.88E-09	5.57E-08	1.3E-09	7.52E-09
Al-TS-1 (100)	1.81E-08	2.24E-09	8.69E-09	3.03E-08	2.6E-10	8.41E-09
Al-TS-1 (50)	5.51E-09	5.06E-10	1.57E-08	2.28E-08	1.23E-10	4.49E-09

Table B12 Data of percentage of selectivity with molar ratio of toluene: H_2O_2 as 2:1 for figure 4.16, Page 42

Selectivity						
Catalyst	**70°C 2:1**			**90°C 2:1**		
	Benzaldehyde	**o-cresol**	**p-cresol**	**Benzaldehyde**	**o-cresol**	**p-cresol**
TS-1 (1D)	0.00	26.10	73.9	8.72	19.28	72.00
TS-1 (3D)	2.42	20.92	76.66	8.64	20.87	70.49
Al-TS-1 (200)	63.96	6.73	29.31	69.13	6.02	24.85
Al-TS-1 (150)	70.88	8.31	20.81	79.94	1.87	18.19
Al-TS-1 (100)	62.41	8.17	29.42	70.71	0.61	28.68
Al-TS-1 (50)	61.92	5.12	32.96	68.42	0.37	31.21

APPENDIX C

CALIBRATION CURVES

This appendix shows the calibration curves for calculation of composition of products in hydroxylation of alkyl benzenes reaction. The main product of hydroxylation of toluene is benzaldehyde and cresol.

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 Figure C1-C3, respectively.

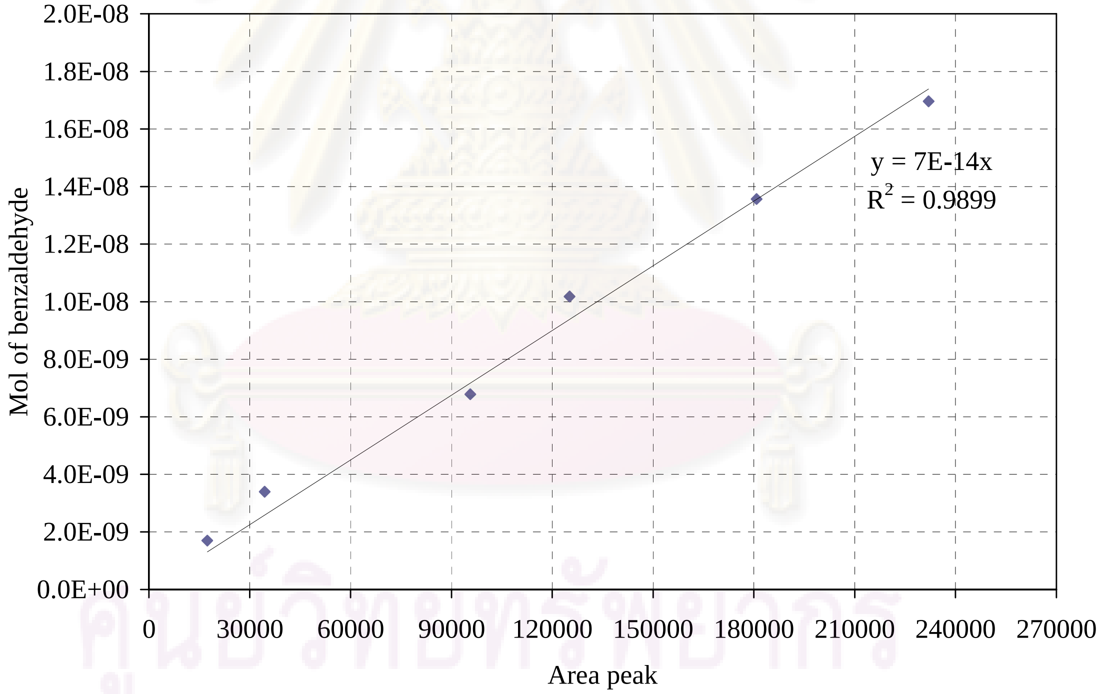


Figure C1 The calibration curve of benzaldehyde.

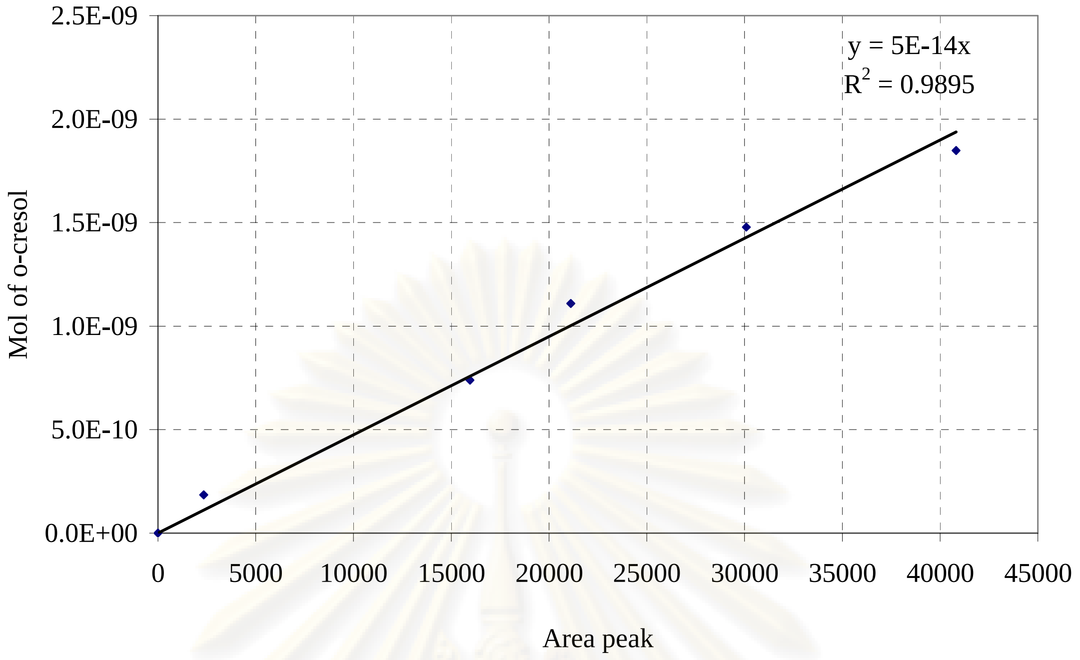


Figure C2 The calibration curve of *o*-cresol.

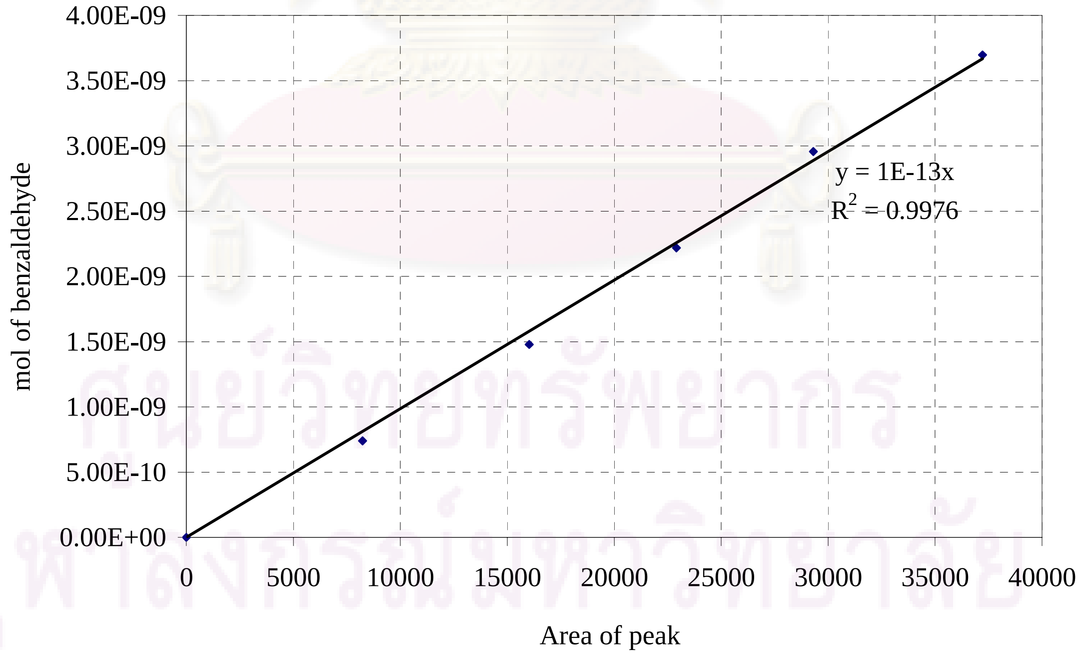


Figure C3 The calibration curve of *p*-cresol.

APPENDIX D

CALCULATION OF CONVERSION SELECTIVITY AND PRODUCT SELECTIVITY

The catalyst performance for the hydroxylation reaction was evaluated in conversion for terms of activity.

1. The percentage of H_2O_2 conversion

$$H_2O_2 \text{ conversion (\%)} = 100 \times \frac{\text{Overall mole of benzaldehyde and cresol}}{\text{Overall mole of } H_2O_2} \qquad \text{(D1)}$$

Where overall mole of product can be measured as follows:

Overall mole of benzaldehyde

$$= \frac{(2\times\text{Mole of benzaldehyde}) \times \text{Total volume of solution before injection into GC-9A}}{\text{Volume of injection into GC-9A}} \qquad \text{(D2)}$$

Overall mole of o-cresol

$$= \frac{\text{Mole of o-cresol} \times \text{Total volume of solution before injection into GC-9A}}{\text{Volume of injection into GC-9A}} \qquad \text{(D3)}$$

Overall mole of p-cresol

$$= \frac{\text{Mole of p-cresol} \times \text{Total volume of solution before injection into GC-9A}}{\text{Volume of injection into GC-9A}} \qquad \text{(D4)}$$

Where mole of benzaldehyde, o-cresol, and p-cresol can be measured employing the calibration curve in Figure C1, C2, and C3 respectively, Appendix C.

Mole of benzaldehyde

$$= ((\text{Area of benzaldehyde peak from integrator plot on GC-9A}) \times 7.0\times10^{-14}) \qquad \text{(D5)}$$

Mole of o-cresol

$$= ((\text{Area of o-cresol peak from integrator plot on GC-9A}) \times 5.0\times10^{-14}) \qquad \text{(D6)}$$

Mole of p-cresol

$$= ((\text{Area of p-cresol peak from integrator plot on GC-9A}) \times 1.0\times10^{-13}) \qquad (D7)$$

Therefore,

Mole of all products

$$= ((2\times\text{mole of benzaldehyde}) + \text{mole of o-cresol} + \text{mole of p-cresol}) \qquad (D8)$$

2. The percentage of product selectivity

Where selectivity of Benzaldehyde can be measured as follows:

$$\%\ \text{Selectivity of Benzaldehyde} = \frac{\text{Mole of Benzaldehyde}}{\text{Mole of all products}} \qquad (D9)$$

Where overall mole of benzene can be measured as follows:

$$\text{Overall mole of toluene} = \frac{\text{Volume of toluene feeding} \times \text{Density of toluene}}{\text{Molecular weight of toluene}}$$

$$= \frac{\text{Volume of toluene feeding} \times 0.903}{92.14} \qquad (D10)$$

3. The percentage of productivity

The productivity of o-cresol

$$\text{Productivity of o-cresol} = \frac{\text{Overall mole o-cresol}}{\text{Weigth catalyst (g)} \times 7200} \qquad (D11)$$

APPENDIX E

CALCULATION FOR CATALYST PREPARATION

The calculation is based on weight of Sodium Silicalite ($Na_2O \cdot SiO_2 \cdot H_2O$) in B1 and B2 solutions.

Molecular Weight of Si = 28.0855

Molecular Weight of SiO_2 = 60.0843

Weight percent of SiO_2 in sodium Silicate = 28.5

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

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

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

$$= 0.3273$$

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

Molecular weight of Ti = 47.88

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

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

Si/Ti atomic ratio = 50

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

= 6.546×10^{-3} mole

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

= 2.2970 g

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

Molecular weight of Al = 26.98

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

Si/Al atomic ratio = 150

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

= 2.18×10^{-3} mole

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

= 0.82 g

which used in A1 and A2 solutions.

APPENDIX F

DATA OF CALCULATION OF ACID SITE

Table F1 Reported total peak area from Micromeritrics Chemisorb 2750.

Sample	**Report total peak area**
TS-1 (1D)	0.0494
TS-1 (3D)	0.0202
Al-TS-1 (200)	0.1539
Al-TS-1 (150)	0.7092
Al-TS-1 (100)	0.1043
Al-TS-1 (50)	0.41752

Calulation of total acid sites

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

1. Conversion of total peak area to peak volume

Conversion from Micromeritrics Chemisorb 2750 is equal to 77.5016 ml/area unit. Therefore, total peak volume is derived from

$$\begin{aligned}\text{Total peak volume} &= 77.5016 \times \text{total peak area}\\ &= 77.5016 \times 0.0494\\ &= 3.8270\ \text{ml}\end{aligned}$$

2. Calculation for adsorbed volume of 15% NH_3

$$\text{Adsorbed volume of 15\% } NH_3 = 0.15 \times \text{total peak volume}$$
$$= 0.15 \times 3.8270 \text{ ml}$$
$$= 0.5741 \text{ ml}$$

3. Total acid sties are calculated from the following equation

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

For TS-1 sample, 0.1005 g of this sample was measured, therefore

$$\text{Total acid sites} = \frac{0.0894 \text{ ml} \times 101.325 \text{ Pa}}{\left(8.314 \times 10^{-3} \frac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}}\right) \times 298 \text{ K} \times (0.1005 \text{ g})}$$

$$= 233.6024 \ \mu\text{mol } H^+/\text{g}$$

Calculation of acid site ratio

As known, the first peak from desorption is indicated as weak acid, relative with another peak and the second one is strong acid. Ratio of each acid site on catalyst surface is calculated from reported peak area of peak fitting program as shown above.

For example, TS-1 sample , the ratio of each acid site on catalyst surface is calculated from the following equation.

$$\text{The ratio of weak acid} = \frac{1^{\text{st}} \text{ peak area}}{\text{summation of both peak areas}} \times 100 \ \%$$

From Figure F6., 1st peak area and 2nd peak area are equal to 0.6887 and 0.0346, respectively.

The ratio of weak acid $= \dfrac{0.6887}{0.6887 + 0.0346} \times 100\ \%$

$= 95.22\ \%$

therefore, the ratio of strong acid $= 100 - 95.22\ \%$

$= 4.78\ \%$

APPENDIX G

CALCULATION OF METAL QUANTITY

Example of the calculation of the metal quantity in catalyst

The XRF results were reported in the amount of metal oxide as shown in table C1

Table G1 Data of TS-1(1) from XRF analysis

Metal oxide	Concentration (% wt)
Al_2O_3	0.058
SiO_2	97.203
CaO	0.03
TiO_2	2.566
Fe_2O_3	0.041

Molecular weights of the metal oxides are shown as follow:

Metal Oxide	Molecular weight (MW)
Al_2O_3	101.9613
SiO_2	60.0843
CaO	56.0774
TiO_2	79.8658
Fe_2O_3	159.6922
CoO	74.9326

1. Mole of metal oxides

$$Mole\ of\ \ Al_2O_3 = \frac{weight\ of\ \ Al_2O_3}{molecular\ weight\ of\ \ Al_2O_3}$$

$$\text{Mole of } Al_2O_3 = \frac{0.058}{101.9613} = 5.69\times10^{-4}\ \text{mole}$$

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

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

$$\begin{aligned} \text{Mole of Al} &= (2) \times (5.69 \times 10^{-4}) \\ &= 0.001707 \text{ mole} \end{aligned}$$

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

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

$$\text{Mole \% of Al} = \frac{0.001707}{6.60317} = 0.000258 \text{ mole\%}$$

Calculated weight%, mole of metal oxide, mole of metal and mole% of cation are illustrated in

Table G2 Calculated composition of TS-1(1D)

TS-1(1)			**mole of metal oxide**	**mole of cation**	**mole % of cation**	**Mol %**
Compound	**% wt**	**MW**				
Al_2O_3	0.058	101.96	5.69E-04	0.0017	0.0003	0.0258
SiO_2	97.203	60.08	1.617777	6.4711	0.98	98.0000
CaO	0.03	56.08	5.35E-04	0.0010	0.0002	0.0162
TiO_2	2.566	79.87	3.21E-02	0.1285	0.0195	1.9463
Fe_2O_3	0.041	159.69	2.57E-04	0.0008	0.0001	0.0117

Table G3 Calculated composition of TS-1(3D)

TS-1(3)			mole of metal oxide	Mole of cation	mole % of cation	Mol %
Compound	% wt	MW				
Al_2O_3	0.072	101.96	7.06E-04	0.0021	0.0003	0.0323
SiO_2	95.99	60.08	1.597589	6.3904	0.9734	97.3410
CaO	0.0199	56.08	3.55E-04	0.0007	0.0001	0.0108
TiO_2	3.418	79.87	4.28E-02	0.1712	0.0261	2.6076
Fe_2O_3	0.029	159.69	1.82E-04	0.0005	0.0001	0.0083

Table G4 Calculated composition of Al-TS-1(50)

Al-TS-1(50)			Mole of metal oxide	mole of cation	mole % of cation	Mol %
Compound	% wt	MW				
Na_2O_3	1.256	61.98	0.0203	0.0405	0.0062	0.6249
Al_2O_3	1.062	101.96	0.0104	0.0312	0.0048	0.4818
SiO_2	92.737	60.08	1.5434	6.1738	0.9519	95.1909
K_2O	0.116	94.20	0.0012	0.0012	0.0002	0.0190
CaO	0.055	56.08	0.0010	0.0010	0.0002	0.0151
TiO_2	4.736	79.87	0.0593	0.2372	0.0366	3.6572
Fe_2O_3	0.038	159.69	0.0002	0.0007	0.0001	0.0110

Table G5 Calculated composition of Al-TS-1(100)

Al-TS-1(100)			mole of metal oxide	mole of cation	mole % of cation	Mol %
Compound	% wt	MW				
Al_2O_3	0.623	101.96	0.0060	0.0183	0.0028	0.2826
SiO_2	96.23	60.08	1.6016	6.4063	0.9878	98.7764
TiO_2	2.973	79.87	0.0372	0.1489	0.0230	2.2958
Fe_2O_3	0.033	159.69	0.0002	0.0006	9.56E-05	0.0096

Table G6 Calculated composition of Al-TS-1(150)

Al-TS-1(150)			mole of metal oxide	mole of cation	mole % of cation	Mol %
Compound	**% wt**	**MW**				
Na_2O_3	0.865	61.98	0.0140	0.0279	0.0043	0.4304
Al_2O_3	0.487	101.96	0.0048	0.0143	0.0022	0.2209
SiO_2	94.151	60.08	1.5670	6.2679	0.9664	96.6423
K_2O	0.113	94.20	0.0014	0.0014	0.0002	0.0218
CaO	0.058	56.08	0.0004	0.0004	5.60E-05	0.0056
TiO_2	3.843	79.87	0.0481	0.1925	0.0297	2.9677
Fe_2O_3	0.039	159.69	0.0002	0.0007	0.0001	0.0113

Table G7 Calculated composition of Al-TS-1(200)

Al-TS-1(200)			mole of metal oxide	mole of cation	mole % of cation	Mol %
Compound	**% wt**	**MW**				
Na	0.833	61.98	0.0134	0.0269	0.0041	0.4144
Al_2O_3	0.451	101.96	0.0044	0.0133	0.0020	0.2046
SiO_2	94.959	60.08	1.5804	6.3217	0.9747	97.4717
K	0.041	94.20	0.0004	0.0004	6.71E-05	0.0067
Ca	0.05	56.08	0.0009	0.0009	0.0001	0.0137
TiO_2	3.63	79.87	0.0455	0.1818	0.0280	2.8032
Fe_2O_3	0.036	159.69	0.0002	0.0007	0.0001	0.0104

APPENDIX H

MATERIAL SAFETY DATA SHEET

Toluene

General

Synonyms: ethenylmethylbenzene, tolylethylene, NCI-C56406, vinyltoluene, 1-methyl-1-phenylethylene
Molecular formula: C_9H_{10}

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.

Hydrogen peroxide

General

Synonyms: Peroxide, 100 volume peroxide, Hydrogen dioxide solution, Hydrogen peroxde, 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 causes serious burns. Eye contact can cause serious injury, possibly blindness. Harmful by inhalation, ingestion and skin contact. Typical OEL 1 ppm.

Hazards Identification

Danger! 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: C_7H_8O

Physical data

Appearance: colourless to light yellow liquid
Melting point: 32 - 34 °C
Boiling point: 191 °C
Vapour density: 3.72
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: $CH_3C_6H_4OH$

Physical data

Appearance: crystals
Melting point: 34 °C
Boiling point: 202 °C
Vapour density: 3.7 (air = 1)
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 °C
Boiling point: 179 °C
Vapour density: 3.6 (air = 1)
Vapour pressure: 1 mm Hg at 26 °C
Density (g cm-3): 1.04
Flash point: 63 °C (closed cup)
Explosion limits: 2.1 - 13.5 %
Autoignition temperature: 192 °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.

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 : 1.486 g/cm^3

Toxicology

Irritating to eyes, respiratory system and skin.

Personal protection

Avoid contact with skin and eyes.

Tetrapropylammonium bromide

General

Synonyms: 1-Propanaminium, N, N, N-tripropyl, bromide or Tetra-n-propylammonium bromide or TPBr or TPABr
Molecular formula: $C_{12}H_{28}N.Br$
Chemical formula : $(C_3H_7)_4NBr$

Physical data

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

Stability and reactivity

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

Hazardous decomposition

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

Potential health effect

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

First aid measure

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

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

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

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

Fire fighting measures

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

Hazardous product combustion

May emit Nitrogen oxides, Hydrobromic acid and Carbon monoxide.

Sodium chloride

General

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

Molecular formula: $NaCl$

Physical data

Appearance : colorless crystals or white powder
Melting point: 804 °C
Boiling point : 1413 °C
Vapor pressure : 1 mm Hg at 865°C
Specific gravity : 2.16 g cm^{-3}
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 : 1390 °C
Vapor pressure : 1 mm Hg at 739 °C
Specific gravity : 2.12 g cm^{-3}
Water solubility : high (Note: dissolution in water is highly exothermic)

Stability

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

Toxicology

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

Personal protection

Safety glasses, adequate ventilation, Neoprene or PVC gloves.

Sodium silicate

General

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

Molecular formula: Na_4O_4Si

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: $Al(NO_3)_3\ 9H_2O$

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 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, vomitting 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.

APPENDIX I

LIST OF PUBLICATION

Pattaraporn Harnvanich, and Tharathon Mongkhonsi "Direct synthesis of benzaldehyde from toluene", The 18th Thailand Chemical Engineering and Applied Chemistry Conference (TiChE 18), Pattaya, Thailand, October, 2008, Page 91.

VITA

Miss Pattaraporn Harnvanich was born on Dec 23rd, 1984 in Ratchaburi, Thailand. She finished high school from Rattanaratbumrung School in 2003, and received the bachelor's degree of Chemical Engineering from Faculty of Engineer, Srinakharinwirot University in 2007. She continued her master's study at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.