ผลของความเป็นกรดของสารละลายต่อปฏิกิริยาระหว่างโทลูอีนและไฮโดรเจนเปอร์ออกไซด์บนตัวเร่งปฏิกิริยาไทเทเนียมซิลิกาไลท์-1

นางสาวนฤมล เกษมสุขไพศาล

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EFFECT OF ACIDITY OF SOLUTION ON REACTION BETWEEN TOLUENE AND HYDROGEN PEROXIDE OVER TS-1 CATALYSTS

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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
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Thesis Title	EFFECT OF ACIDITY OF SOLUTION ON REACTION BETWEEN TOLUENE AND HYDROGEN PEROXIDE OVER TS-1 CATALYSTS
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นฤมล เกษมสุขไพศาล : ผลของความเป็นกรดของสารละลายต่อปฏิกิริยาระหว่างโทลูอีนและไฮโดรเจนเปอร์ออกไซด์บนตัวเร่งปฏิกิริยาไทเทเนียมซิลิกาไลท์-1. (EFFECT OF ACIDITY OF SOLUTION ON REACTION BETWEEN TOLUENE AND HYDROGEN PEROXIDE OVER TS-1 CATALYSTS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.ธราธร มงคลศรี, 98 หน้า.

งานวิจัยนี้ทำการศึกษาผลของความเป็นกรดของสารละลายต่อปฏิกิริยาระหว่างโทลูอีนและไฮโดรเจนเปอร์ออกไซด์โดยใช้ตัวเร่งปฏิกิริยาไทเทเนียมซิลิกาไลต์-1 และไทเทเนียมซิลิกาไลต์-1 ที่ได้รับการปรับปรุงด้วยโลหะโคบอลต์ในปริมาณต่าง ๆ ตัวเร่งปฏิกิริยาเตรียมด้วยวิธีไฮโดรเทอร์มอลและทำการวิเคราะห์คุณลักษณะด้วย XRD, FT-IR, XRF, BET และ NH_3-TPD ทำปฏิกิริยาที่อุณหภูมิ 70 และ 90 องศาเซลเซียส ในเครื่องปฏิกรณ์แบบปั่นกวน การเติมกรดไฮโดรคลอริกในเฟสของเหลวเพื่อช่วยลดการสลายตัวของไฮโดรเจนเปอร์ออกไซด์ก่อนที่จะทำปฏิกิริยากับโทลูอีน ผลที่ได้จากการศึกษาความว่องไวในการทำปฏิกิริยาพบว่าตัวเร่งปฏิกิริยาทุกตัวให้ผลิตภัณฑ์เป็นเบนซาลดีไฮด์ ออโธ-ครีซอล และพารา-ครีซอล ปฏิกิริยาที่มีการเติมกรดไฮโดรคลอริกให้ค่าการเกิดผลิตภัณฑ์สูงกว่าปฏิกิริยาที่ไม่มีการเติมกรดไฮโดรคลอริก การเติมกรดทำให้ค่าการเลือกเกิดออโธ-ครีซอลและพารา-ครีซอลลดลง แต่ทำให้การเกิดเบนซาลดีไฮด์เพิ่มสูงขึ้น และเมื่อเพิ่มปริมาณของกรดไฮโดรคลอริกที่เติมลงไปพบว่า ค่าร้อยละการเปลี่ยนแปลงของไฮโดรเจนเปอร์ออกไซด์เพิ่มขึ้นเมื่อเพิ่มปริมาณกรดจนถึงระดับหนึ่ง จากนั้นเมื่อเพิ่มปริมาณของกรดไฮโดรคลอริกพบว่าให้ค่าร้อยละการเปลี่ยนแปลงของไฮโดรเจนเปอร์ออกไซด์ที่ลดลง

ภาควิชา..............วิศวกรรมเคมี.............. ลายมือชื่อนิสิต นฤมล เกษมสุขไพศาล
สาขาวิชา............วิศวกรรมเคมี............... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก..................
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NARUMON KASEMSUKPHAISAN: EFFECT OF ACIDITY OF SOLUTION ON REACTION BETWEEN TOLUENE AND HYDROGEN PEROXIDE OVER TS-1 CATALYSTS. THESIS ADVISOR: ASSOC.PROF. THARATHON MONGKHONSI, Ph.D., 98 pp.

This research studies effect of acidity of solution on reaction between toluene and hydrogen peroxide using titanium silicalite-1 (TS-1) and TS-1 modified with different amount of Co catalysts. The catalysts are prepared by a hydrothermal method and characterized by XRD, FT-IR, XRF BET and NH_3-TPD. The reaction is carried out at reaction temperature 70 and 90 °C in a stir slurry reactor. Hydrochloric acid is added to the liquid phase to decrease the self decomposition of hydrogen peroxide before reacting with toluene. Catalytic activity testing found that the reactions added with hydrochloric acid have higher conversion than reactions which no acid for all the catalysts studied. In addition, the addition of hydrochloric acid slightly decreases the productivity of o-cresol and p-cresol but significantly increases the formation of benzaldehyde. The conversion increases with the increase amount of hydrochloric acid added up to a level. Beyond that point the conversion decreases if the amount of hydrochloric acid added is further increased.

Department : Chemical Engineering Student's Signature นฤมล เกษมสุขไพศาล
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Last of all, I would like to dedicate the achievement of my work to my family. Without their love, support, encouragement, and understanding to me in the difficult times, I do not know if I would be able to finish this work ever.

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CHAPTER I

INTRODUCTION

Cresol is an organic compound which has a methyl group substituted onto the benzene ring of a phenol molecule. There are three forms of cresols that are only slightly different in their chemical structure: ortho-cresol (o-cresol), meta-cresol (m-cresol) and para-cresol (p-cresol). Cresols have a wide variety of uses including the manufacture of synthetic resins, tricresyl phosphate, salicylaldehyde and herbicides. Cresol solutions are used as household cleaners, disinfectants and important chemical raw material.

The oldest cresol production method used in the United States is through the recovery of fractional distillates from coal tars. Most domestic cresols are formed via catalytic and thermal cracking of naphtha fractions during petroleum distillation. Since 1965, quantities of coal tar and petroleum have been insufficient to meet the rising demand. Consequently, several processes for the manufacture of the various isomers have been developed. At present, cresol is mainly produced from the methyl alkylation of phenol process which produces a mixture of anisol and mixed cresol (ortho-, meta- and para-cresol). Beginning from aromatic reactant, the current route also has another drawback it consists of two steps: (1) the conversion of benzene to phenol via the cumene process or the hydroxylation of benzene to phenol (2) the methanol alkylation of phenol process to produce cresol. The several steps in reaction is the disadvantage of this process and cumenehydroperoxide is unstable, its may be danger for process. The route to produce cresol is shown in **Figure 1.1.**

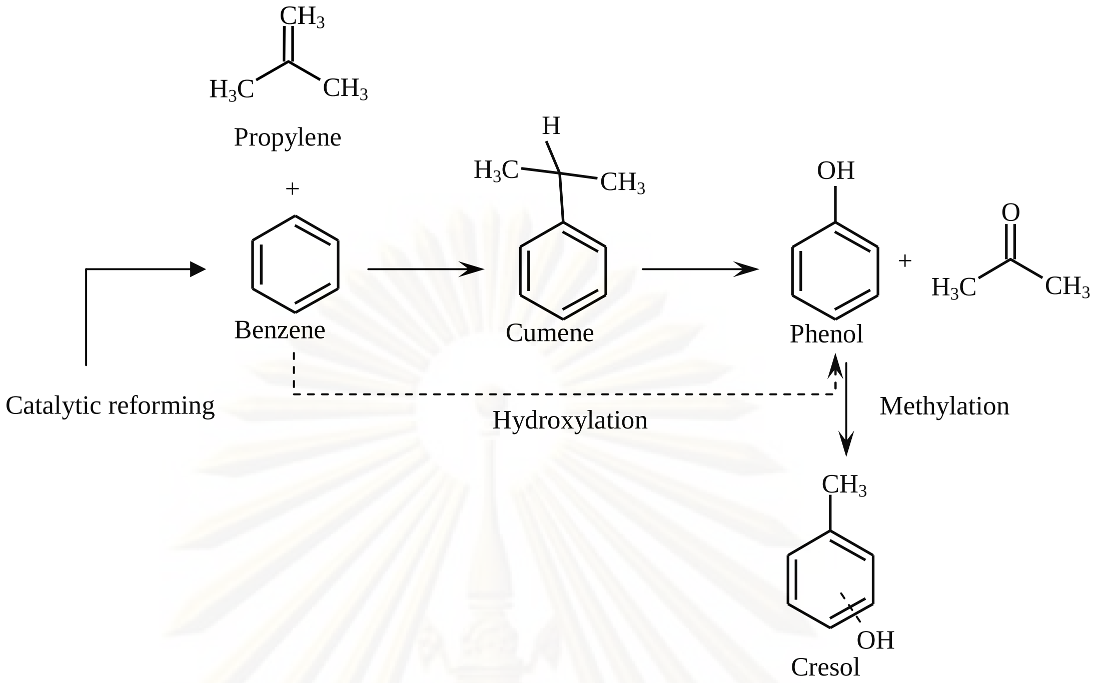


Figure 1.1 The route to produce cresol

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 acetate 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 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. The route to produce benzaldehyde is shown in **Figure 1.2.**

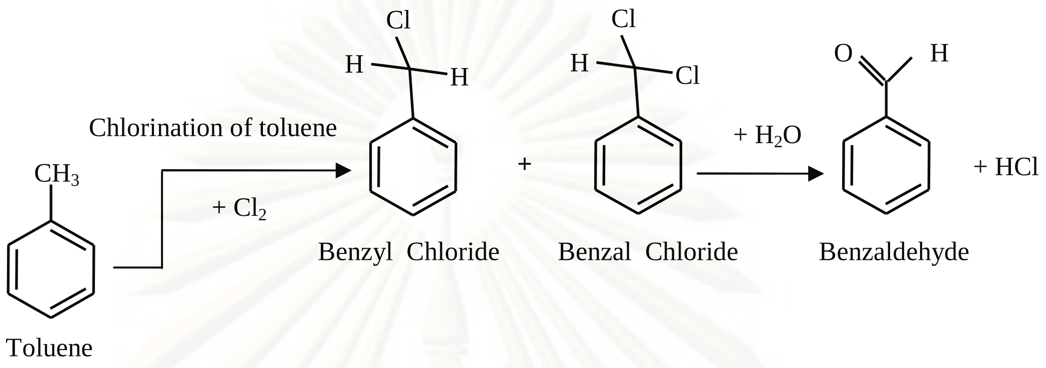


Figure 1.2 The route to produce benzaldehyde

It can be obviously seen from the above paragraphs that there is no common production step between the production of cresols and benzaldehyde. In our previous researches (Rojarek Passasadee, 2008 and Pattaraporn Harnvanich, 2008), however, it is found that the reaction between toluene as reactant and H_2O_2 as oxidant can produce either benzaldehyde or cresols or both by using an appropriate catalyst (see **Figure 1.3**). The catalyst found to have the above property is TS-1 and TS-1 modified with a suitable second metal. For example, if TS-1 is modified by adding Co (Co-TS-1), either cresols and/or benzaldehyde will become the prominent products depends on the reaction temperature. In some cases, especially at a low reaction temperature, cresols is the only reaction products formed (Rojarek Passasadee, 2008). If TS-1 is modified by adding Al (Al-TS-1), benzaldehyde will become the prominent products with a lesser amount of cresols, and in several cases the only product formed (Pattaraporn Harnvanich, 2008).

The advantage of the new route is only one process is required for the production of cresols or benzaldehyde and the reaction complete in only one step. The only thing has to be changed is the catalyst used. This offers process flexibility.

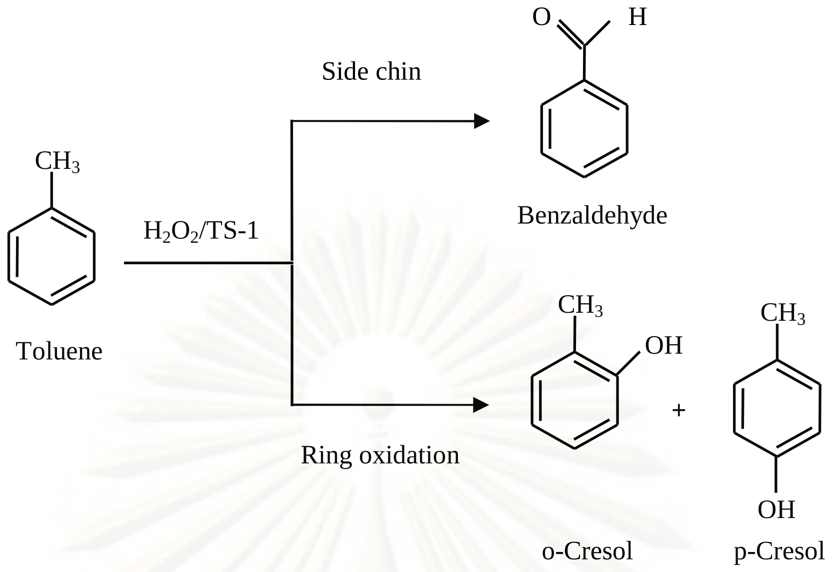


Figure 1.3 Hydroxylation of toluene by use hydrogen peroxide as oxidant over titanium silicalite-1 catalyst

This process, however, still has a drawback that is the conversion is rather low. A possible cause is H_2O_2 decompose rather than reacting with toluene. Hydrogen peroxide always decomposes exothermically into water and oxygen gas spontaneously according to the equation: $2H_2O_2 \rightarrow 2H_2O + O_2$. This decomposition process is very favorable thermodynamically. The rate of decomposition depends on the temperature and concentration of the peroxide, as well as the pH and the presence of impurities and stabilizers. Choudhary et al. (2006) had study factors influencing decomposition of hydrogen peroxide over supported Pd catalyst in aqueous medium. They found that adding acid in aqueous medium decreased the hydrogen peroxide decomposition activity in the following order: hydroiodic acid > hydrobromic acid > hydrochloric acid > acetic acid > phosphoric acid > sulfuric acid > perchloric acid and the ability of decreasing the hydrogen peroxide decomposition activity depend on the concentration acid in aqueous medium.

Another drawback is the cost of hydrogen peroxide is high. Therefore, any attempt that can attenuate the decomposition of hydrogen peroxide is a way to use its worth. Because of these facts, the present work is set up to study the possibility of using the technique present by Choudhary et al. (2006), adding acid, to decrease the decomposition of hydrogen peroxide during the hydroxylation of toluene. It is expected that if the self-decomposition of H_2O_2 can be reduced, the utilization of H_2O_2 can be raised up.

The first question has to be answered is which catalyst should be used in this research. To see the effect(s) of acidity on the products formed, the catalyst used should be able to produce cresols and benzaldehyde. Since Co-TS-1 can produce either cresols or benzaldehyde as the main product while Al-TS-1 produces only benzaldehyde as the main product, Co-TS-1 is selected to be the representative catalyst in this research.

The second question has to be answered is which acid should be used in this research. It is knows that any anion having an atom having highly positive charge (e.g. S in SO_4^{2-} and N in NO_3^-) can replace a hydrogen atom from the benzene ring. This is the unwanted reaction in this research. Therefore, HX (when X is halogen) is chose in this research. The HX used is HCl due to it is widely available and easy to handle.

This research studies the effects of acidity of solution on the reaction between toluene and hydrogen peroxide by using TS-1 catalysts and TS-1 which are modified with cobalt (which will be named Co-TS-1). The research has scope following as:

1) Use TS-1 and TS-1 modified by adding Co with several ratio (Si/Co: 200, 150, 100 and 50) on the hydroxylation of toluene in stirred slurry reactor under triphase condition. All catalysts are prepared by hydrothermal method.

2) Characterization of the synthesized TS-1 catalysts by using the following techniques.

- Determination of crystallinity and structure of catalysts by X-ray diffractometor (XRD).
- Determination of chemical composition of catalysts by X-ray fluorescence (XRF).

- Determination the surface area by N_2 adsorption based on BET method (BET).
- Determination of incorporation of Ti atoms as a framework element by IR Spectroscopy (IR).
- Determination of acid sites of the synthesize catalysts by NH_3-TPD technique.

3) Evaluated catalytic behavior of the synthesized catalysts [TS-1, Co-TS-1(50), Co-TS-1(100), Co-TS-1(150) and Co-TS-1(200)] by using three phase hydroxylation of toluene using hydrogen peroxide as an oxidant in a stirred slurry reactor at 70 °C and 90 °C.

4) Investigate the influence of concentration of acid in solution by carry out the reaction without and with different amount of acid (HCl) in the aqueous H_2O_2 phase.

This present work is organized as follows:

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

Chapter II reviews the theory of this research and literature on the catalytic activity of metal modified TS-1 catalysts in the hydroxylation of toluene reaction.

Chapter III consists of catalyst preparation, catalyst characterization and catalytic reaction between toluene and H_2O_2.

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 from this research and some recommendation for future work.

CHAPTER II

THEORY AND LITERATURE REVIEWED

2.1 The decomposition of hydrogen peroxide

Hydrogen peroxide (H_2O_2 or H-O-O-H) is a very pale blue liquid, appears colorless in dilute solution, slightly more viscous than water. It is weakly acidic in aqueous solution. As a weak acid, hydrogen peroxide forms salts with various metals (Hess, 1995). For consumers, it is usually available from pharmacies at 3 or 6 wt. % concentrations and 30 wt. % concentrations for most common laboratory use. Hydrogen peroxide has strong oxidizing and reducing properties, as an oxidizer in controlling sulfide and organic related odors in wastewater collection and treatment systems and is a powerful bleaching agent for the textile and pulp/paper industry replace to chlorine-based bleaches which highly corrosive to metal. It is used as a disinfectant, antiseptic, propellant in rocketry and also in chemical syntheses.

Decomposition of hydrogen peroxide occurs with proportionate: $2H_2O_2 \rightarrow 2H_2O + O_2$ and is extremely important in handling hydrogen peroxide during storage and in the laboratory. This reaction is highly exothermic and takes place in the presence of small amounts of catalyst of catalyst even in aqueous solution. In the absence of catalyst, it occurs only gas phase at high temperature. Hydrogen peroxide is incompatible with many substances that catalyze its decomposition, including most of the transition metals and their compounds. Decomposition can be catalyzed both homogeneously by dissolved ions (especially of the metals iron, copper, manganese, and chromium) and heterogeneously by suspended oxides and hydroxides (e.g., those of manganese, iron, copper, palladium, or mercury) and by metals such as platinum, osmium, and silver. Common catalysts include manganese dioxide, and silver. In the presence of certain catalysts, such as Fe^{2+} or Ti^{3+}, the decomposition may take a different path, with free radicals such as HO· and HOO· being formed. A combination of H_2O_2 and Fe^{2+} is known as “Fenton's reagent” that is used to oxidize contaminants or waste waters. Not only that the rate of decomposition is dependent on the temperature and pH of medium. The decomposition occurs more rapidly in alkali, so acid is often added as a stabilizer.

Hydrogen peroxide is commercially available in aqueous solutions of 30 wt% or 90 wt% concentration. The 30 wt% hydrogen peroxide is a colorless liquid and it is stabilized against decomposition, which occurs in the presence of traces of iron, copper, aluminium, platinum, and other transition metals. The 30 wt% hydrogen peroxide does not mix with nonpolar organic compounds. The 90 wt% hydrogen peroxide is stable at 30°C (the decomposition rate is 1%/year), it decomposed slowly at high temperatures and rapidly with boiling at 140 °C. The pure hydrogen peroxide solution is stable with weak decomposition. However, when it comes in contact with heavy metals or various organic compounds, or mixes with impurities, it produces oxygen gas and decomposition heat (Cholada Komintarachat, 2005).

2.2 Electrophilic aromatics substitution

Benzene is an aromatic having a cyclic conjugated compound with 6 π electron as shown in **Figure 2.1**. The π electrons are more involved in holding together carbon nuclei than are the π electron of a carbon-carbon double bond. The π electrons are loosely held and are available to reagent that is seeking electron. Therefore, benzene ring serves as a source of electron. Benzene reacts mainly with electrophilic reagents. The reaction of benzene ring is called "Electrophilic substitution reactions"

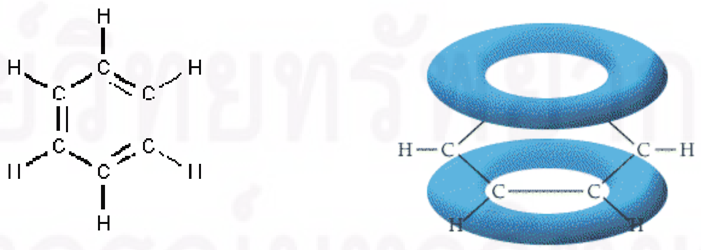


Figure 2.1 Electron cloud of benzene

Electrophilic aromatic substitution replaces a proton on benzene with another electrophile. Electrophilic aromatic substitution includes a wide varity of reaction:

nitration, halogination, sulfonation and Friedel–Crafts reaction. The mechanism of electrophilic aromatic substutition consists of two steps (as shown in **Figure 2.2**)

Step 1: The ring is attacked by electrophilic reagent to form a carbocation

Step 2: The abstraction of a proton from carbocation by some base. In each case there is a preliminary acid – base reaction which generates the attacking particle; the actual substitution.

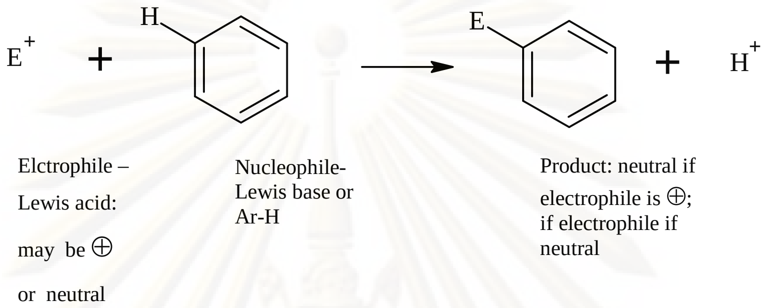
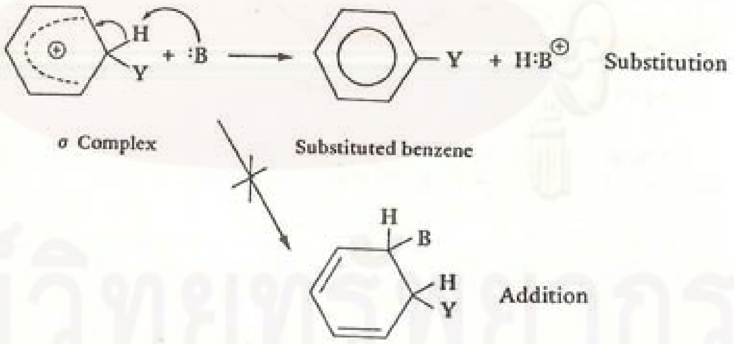


Figure 2.2 The mechanism of electrophilic aromatic substitution

Abstraction of the proton. By abstraction of the α proton with a base the ring system regains its aromatic state. Thus *rearomatization* rather than the addition of the base occurs.



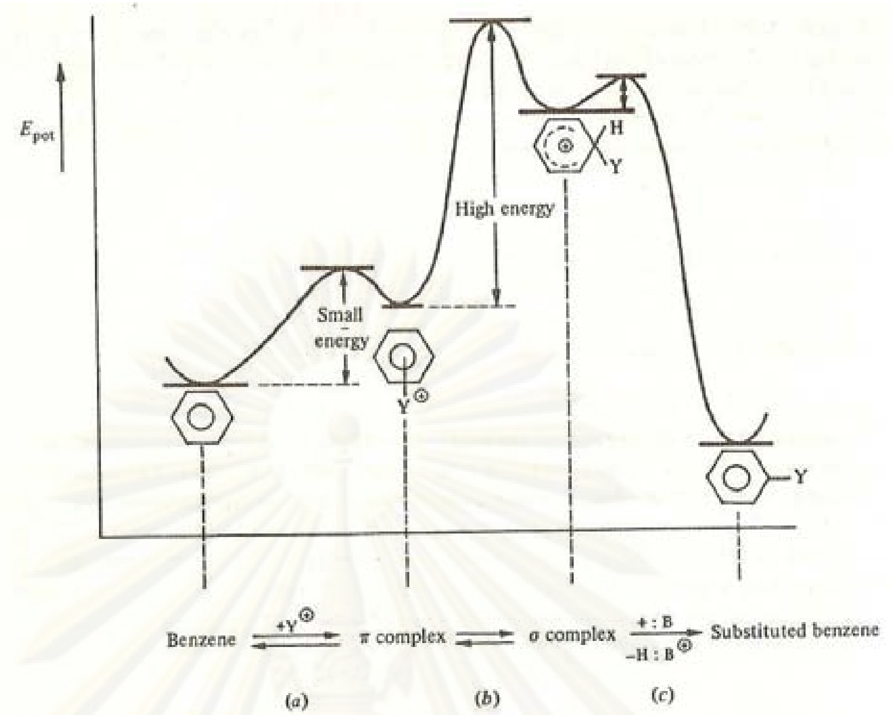


Figure 2.3 Energy profile of electrophilic aromatic substitution on benzene ring (Zlatkis et al., 1985)

This step requires only a small E_{act}, and is exothermic. The energy profile in **Figure 2.3** summarizes the energetic course of an electrophilic aromatic substitution on benzene.

2.2.1 Substituent effects in aromatic rings

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 *met*a director.

2.2.2 Theory of reactivity

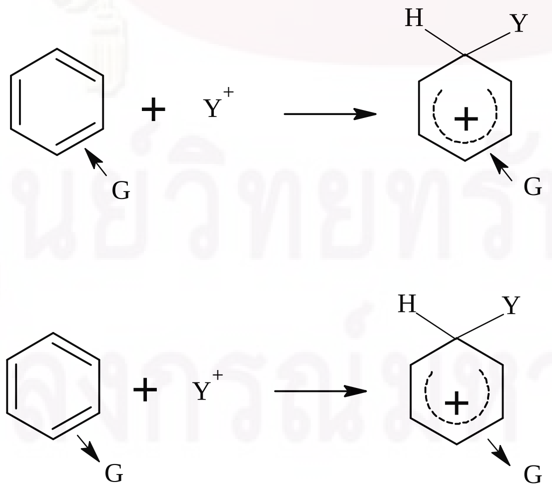
The activity of substituted benzene depends on type of substituent group. The group that releases electrons activates the ring is called “activating group”. The group that withdraws electrons deactivates the ring called “deactivating group”.

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 substituent. 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 2.4** shows type of substituent group.



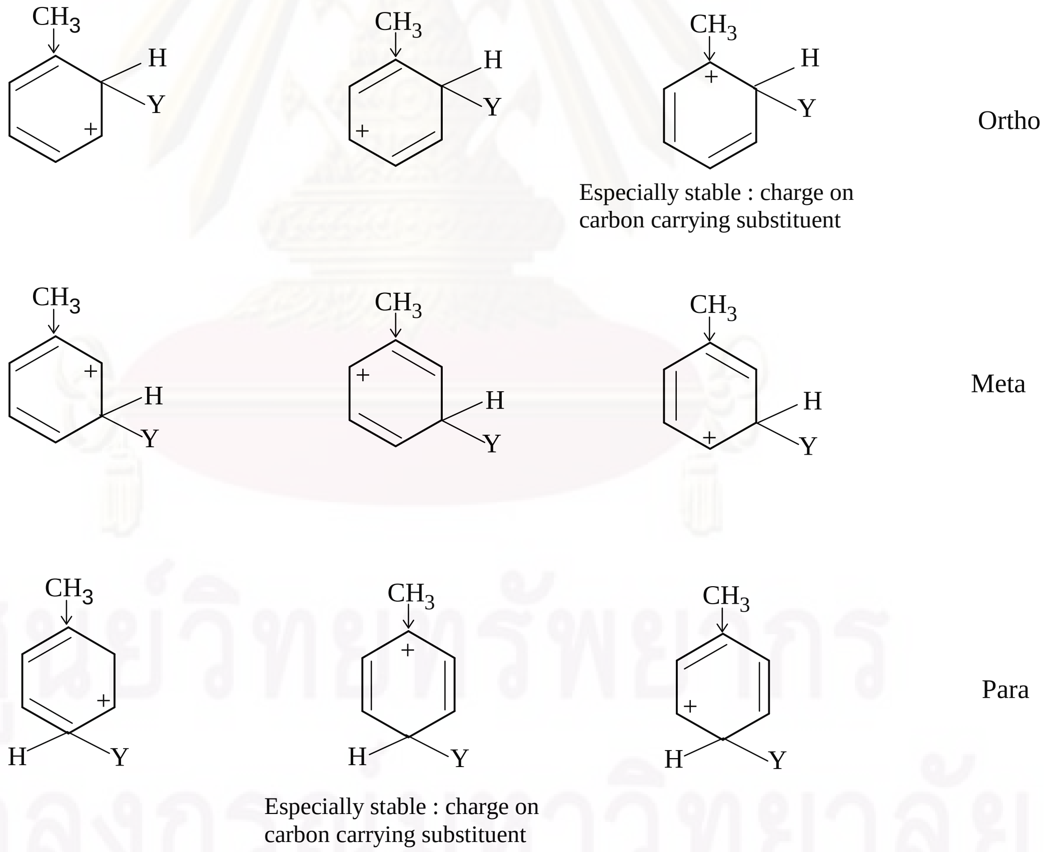
G = release electrons :
stabilizes carbocation,
activates

G = withdraws electrons :
destabilizes carbocation,
deactivates

Figure 2.4 Type of substituent group in electrophilic aromatic substitution

2.2.3 Theory of orientation

The activating group activates all position of the benzene ring; even the positions *meta* but at *ortho* and *para* position much more activates than meta position. The deactivating group deactivate all positions in the ring; even the positions meta but at the position meta much more deactivate than *ortho* and *para* position considering **Figure 2.5** activating group substituent at position *ortho*, *para* and *meta*. The *ortho* and *para* position, 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. The structure that the positive charge located at the same position of –CH_3 make this structure most stable because the electrons from –CH_3 transfer to the ring faster than another structure. In other hand, the *meta* position does not have the structure that make substituted ring stable.

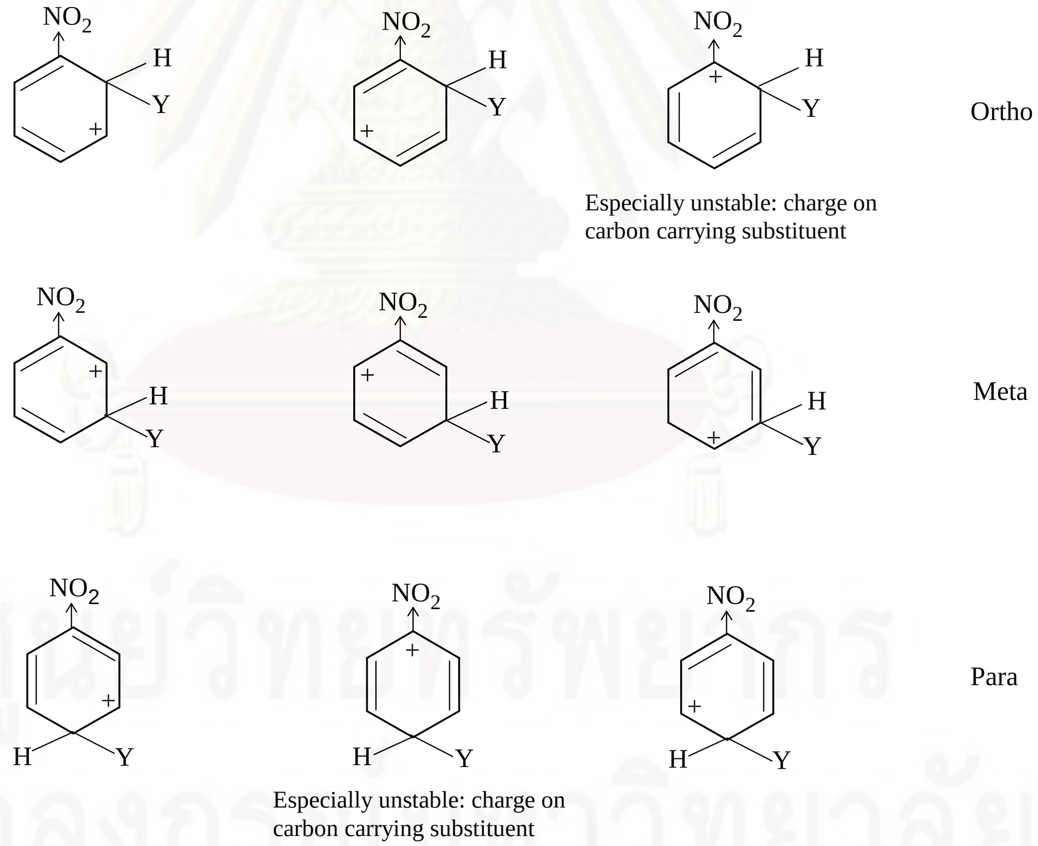


Especially stable : charge on carbon carrying substituent

Especially stable : charge on carbon carrying substituent

Figure 2.5 Activating group substituent at position orho, para and meta

In case of the substitution of nitrobenzene, this compound contains a deactivating group. The substitution at position *ortho* has a three hybrid structures. The positive charge is located on the carbon atom to which $–NO_2$ is attached. Although $–NO_2$ withdraws electrons from all position, it does so most from the carbon atom nearest it. And this carbon atom, already positive, has little tendency to accommodate the positive charge of the carbocation. The last structure at *ortho* position is particularly unstable and does little to stabilize the ion resulting from attack at *ortho* position. The ion for *ortho* attack is virtually a hybrid for two carbon atoms which is less stable than the ion resulting from attack at a *meta* position because *meta* position has a hybrid of three structure and in which the positive charge is accommodated by three carbon atoms. The substitution of *ortho* occurs more slowly than *meta* substitution. In case of position *para* is same as position *ortho*. The mechanism of deactivating group is showed in **Figure 2.6.**



Especially unstable: charge on carbon carrying substituent

Especially unstable: charge on carbon carrying substituent

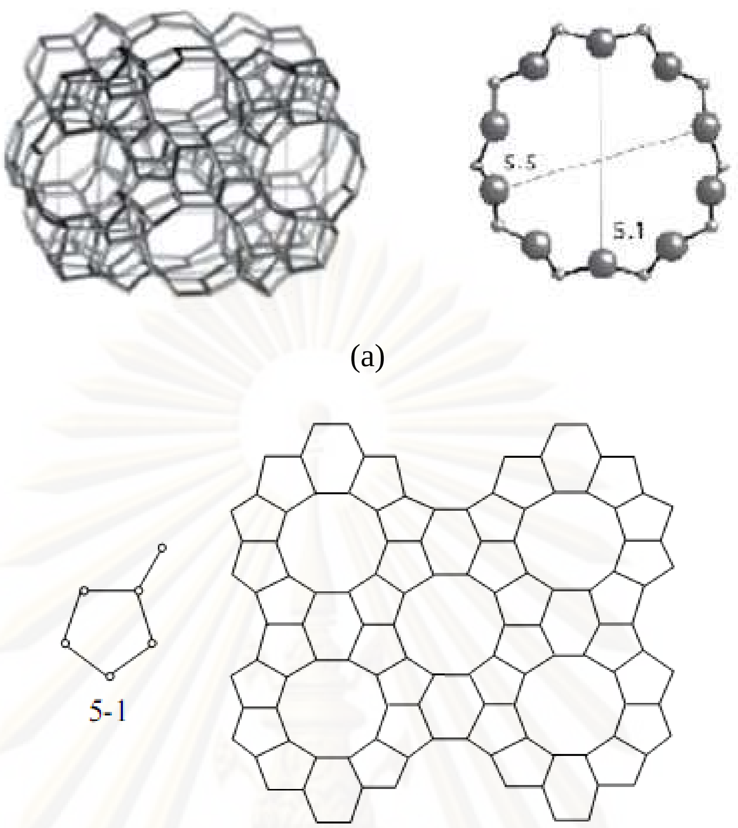
Figure 2.6 Deactivating group substituent at position ortho, para and meta

2.3 Titanium silicalite – 1

Titanium Silicalite-1(denoted TS-1) was discovered in 1983 by Taramasso. 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-1 is a crystalline material in which tetrahedral [TiO_4] and [SiO_4] units are arranged in a MFI structure. The MFI structure is a common pattern of crystalline zeolite that is built up by 5-1 secondary building unit (SBU: the smallest number of TO_4 units, where T is Si or Al but in case of TS-1 at T position is replacing with Si or Ti, from which zeolite topology is built) which are link together to form chain and the interconnection of these chains leads to the formation of the channel system in the structure. The MFI structure has a three dimensional pore system consisting of sinusoidal 10-ring channels (5.1 × 5.5 Å) and intersecting straight 10-ring channels (5.3 × 5.6 Å) (Tosheva et al., 1999). The MFI structure shows in **Figure 2.7.**

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



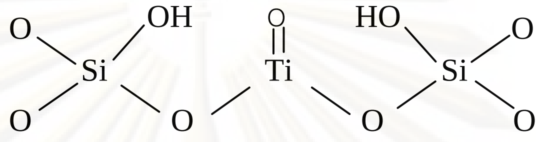
(a)

(b)

Figure 2.7 (a) MFI structure in three dimensional and (b) a 5-1 secondary building unit

From the crystalline structure and the regular change in unit cell parameters which are consistent with isomorphous substitution of Si^{4+} with Ti^{4+} it seems justified to represent TS-l as a silicalite in which few Ti^{4+} have taken the place of Si^{4+}. The interpretation of the catalytic activity of TS-l must take into consideration the role played by these few Ti^{4+}: in fact pure silicalite is totally inactive, and other phases containing Ti have not been identified. Due to the fact that TS-l crystallizes from a homogeneous solution, it is reasonable to assume that the distribution of Ti^{4+} in the crystal lattice is at random; since the silicon/titanium ratio is in the range 40 - 90 in typical preparations, most Ti^{4+} must be isolated from each other by long sequences of -O-Si-O-Si-O-. If Ti^{4+} replaces a Si^{4+} it should be tetrahedrally coordinated by O= however, the presence of a band at 980 cm^{-1} closely corresponds to the band observed in other titanium compounds containing the $>$Ti = O group, whose stretching frequency is 975 cm^{-1} with bond distances of 1.66 – 1.79 Å; furthermore, hydroxyl groups are present at the surface as shown by the increase in selectivity.

Finally, near neighbour positions of Ti^{4+} are occupied by Si^{4+} which in a field of O= is stable only in tetrahedral coordination. A simple representation of the sites where substitution has occurred which takes into consideration the various pieces of experimental evidence could be:



The amount of titanium positioned within the framework of the molecular sieve is believed to be important and beneficial in many reactions. However, it is also widely believed that non-framework Ti-species, on the exterior or interior surfaces of crystals may decrease the catalytic effectiveness of titanium-silicate molecular sieves. Similar deleterious effects may be caused by other contaminants such as aluminum and alkali elements. In particularly, extra-framework massive Ti-oxides as well as other contaminants cause undesirable side reactions and consequence losses of activity and selectivity of the catalyst.

2.4 Related literature review

Hydrogen peroxide is an effective oxidant that could be used in many industrial processes because the only by-product of oxidation using hydrogen peroxide is water, it could become the ultimate green chemical for the manufacture of many oxygenated petrochemicals. Many researchers have applied hydrogen peroxide to several reactions such as Kumar et al. (1999) studied the hydroxylation of aromatics (such as benzene, toluene, anisole and benzyl chloride) over TS-1/H_2O_2, Wang et al. (2003) studied the propylene epoxidation, Pornnapa Kasemsiri (2007) searching for new routes to phenol on direct benzene oxidation replace the cumene process. A potential route is the hydroxylation of benzene by hydrogen peroxide and used TS-1 and TS-1 modified with second metals as catalyst in the slurry reactor. In

2008, Rojarek Passasadee had study in the hydroxylation of toluene by hydrogen peroxide and used TS-1 and Co-TS-1 in the slurry reactor.

The titanium silicalite was first synthesis by Taramasso et al. (1983). They found that TS-1 has a composition corresponding to the formula $xTiO_2(1\text{-}x)SiO_2$. The TS-1 is of the silicalite type, and all the titanium substitutes the silicon. The classical method used tetra methyl ammonium hydroxide (TPAOH) as the template that gives TiO_2 phase in the TS-1 structure. The TiO_2 in anatase phase can decompose H_2O_2 and should be avoid in synthesis titanium silicalite-1. Li et al. (2001) had synthesized titanium silicalite by hydrothermal method. They found 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 tetrapropylammoniumbromide (TPABr) as template differed from that using the classical method (the classical method used TPAOH as the template). But, the symmetry of titanium silicalite changed from monoclinic to orthorhombic with the increase of titanium content in both methods. They found that TS-1 synthesized using TPABr as template did not contain anatase, this kind of $Ti–O_2$ is very stable and cannot be catalytic active site.

Some researchers tried to add another metal to improve catalytic activity of TS-1. Pirutko et al. (2001) synthesized titanosilicalite TS-1 samples modified by Al, V, Cr, Fe, Co and Ru as another metal and all samples were tested in the oxidation of benzene to phenol. They found that all samples still had structure like TS-1 and Fe-TS-1 could catalyze the oxidation of benzene to phenol with high activity and selectivity. Pornnapa Kasemsiri (2007) studied the catalytic performances of TS-1 and TS-1 modified with second metals (Al, Co, V and Fe) in the hydroxylation alkyl benzene as toluene and ethyl benzene. The results of toluene hydroxylation at 70 °C for 2 h showed that all catalysts produced reaction products as p-cresol, o-cresol, particularly TS-1 modified with Al and Fe also had benzaldehyde as predominant product. When the reaction temperature was increased to 95 °C, it had benzaldehyde as major product accompany with p-cresol, o-cresol for using all catalysts (except Fe-TS-1). The second metals affected the products production of toluene hydroxylation at 70 °C and 95 °C i.e. Co and V restrained benzaldehyde production while Al and Fe promoted the formation of benzaldehyde as main reaction product. Rojarek Passasadee (2008) studied the synthesis of cresol in a one-step reaction from toluene and hydrogen peroxide using titanium silicalite-1 (TS-1) catalysts modified with different amount of Co. The reaction is carried out at reaction temperature 70 °C and 90 °C, and toluene per hydrogen peroxide molar ratios 1:1 and 2:1. The catalytic activity testing found that all modified catalysts yield o-cresol and p-cresol as the major products with benzaldehyde as by products. Selectivity toward cresols 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.

2.5 Comments on previous studies

Despite the fact that the hydroxylation of benzene to phenol by H_2O_2 has been widely studied, the reaction between H_2O_2 and toluene is limited to some groups. Many attempts have been made (e.g. catalyst modification, the use of solvent to homogenize the reactants) to improve the productivity of the reaction, but there are several parameters had yet to be explored.

One such parameter is the pH of the aqueous phase. It is known that the pH of the aqueous phase can manipulate the behaviour of H_2O_2. For example, H_2O_2 decomposed slower when pH is less then 7. It is, therefore, interesting to inventive the effect of pH on the reaction system. To the best of our knowledge, this effect has never been studied before.

CHAPTER III

EXPERIMENTAL

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

3.1 Catalyst preparation

3.1.1 Chemicals

All chemicals used in this preparation procedure of TS-1 and Co-TS-1 catalysts are following in **Table 3.1**.

Table 3.1 The chemicals used in the catalyst preparation and reaction

Chemical	Grade	Supplier
Titanium(IV) butoxide 98%	-	Aldrich
Tetrapropylammonium bromide 98%	-	Aldrich
Sodium chloride	Analytical	Ajax
Sodium hydroxide	Analytical	Merck
Sulfuric acid 99%	Analytical	Aldrich
Sodium silicate solution	Extra pure	Merck
Cobalt(II)nitrate hexahydrate	Analytical	Aldrich
Toluene 99.9%	-	Merck
Hydrogen peroxide 30%	-	Merck
Ethanol 99.9%	-	Merck

3.1.2 Preparation procedures

The preparation procedure of Co-TS-1 by rapid crystallization method is shown in **Figure 3.1** and the reagents used are shown in **Table 3.2**.

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

Solution for the gel preparation			Solution for decant-solution preparation		
Solution A1			Solution A2		
Ti[O(CH$_2$)$_3$CH$_3$]$_4$	2.2970	g	Ti[O(CH$_2$)$_3$CH$_3$]$_4$	2.2970	g
TPABr	5.72	g	TPABr	7.53	g
NaCl	11.95	g	De-ionized water	60	ml
Co(NO$_3$)$_2$.6H$_2$O (Si/Co= 50)	1.9051	g	Co(NO$_3$)$_2$.6H$_2$O (Si/Co= 50)	1.9051	g
(Si/Co= 100)	0.9525	g	(Si/Co= 100)	0.9525	g
(Si/Co= 150)	0.6350	g	(Si/Co= 150)	0.6350	g
(Si/Co= 200)	0.4763	g	(Si/Co= 200)	0.4763	g
De-ionized water	60	ml	H_2SO_4 (conc.)	3.4	ml
H_2SO_4 (conc.)	3.4	ml			
Solution B1			Solution B2		
Sodium silicate	69	g	Sodium silicate	69	g
De-ionized water	45	ml	De-ionized water	45	ml
Solution C1			Solution C2		
TPABr	2.16	g	NaCl	26.27	g
NaCl	40.59	g	De-ionized water	104	ml
NaOH	2.39	g			
De-ionized water	208	ml			
H_2SO_4 (conc.)	1.55	ml			

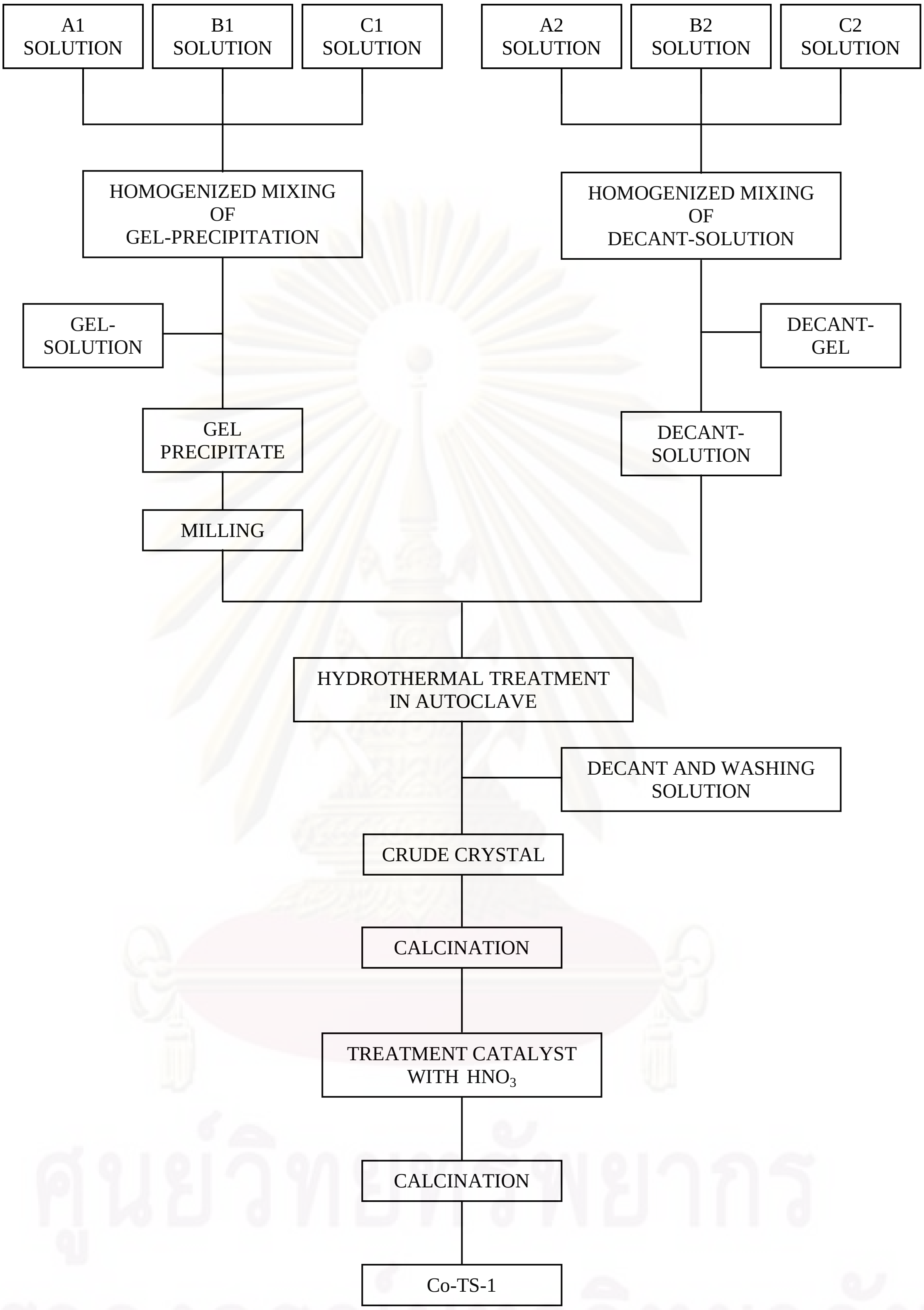


Figure 3.1 The preparation procedure of Co-TS-1 by hydrothermal method

3.1.2.1 Preparation of gel precipitation and decantation Solution

The source of metals for preparation of decantation and gel solutions are $Co(NO_3)_2.6H_2O$ for Co, $Ti[O(CH_2)_3CH_3]_4$ for Ti, and sodium silicate for Si, respectively. TPABr (Tetra-n-propyl ammonium bromide $[(CH_3CH_2CH_2)_4N]Br$) is used as organic template. The atomic ratio of Silicon/Titanium set at 50 and Silicon/Cobalt are set at 200, 150, 100 and 50 respectively. The preparation of supernatant liquid is separated from the gel, which is important for preparing the uniform crystals.

The detail procedures are as follows: firstly, a gel mixture is prepared by adding solution A1 and solution B1 into solution C1 dropwise with vigorous stirring using a magnetic stirrer at room temperature. The pH of the gel mixture is maintained within the range 9-11 because this pH range is suitable for precipitation. H_2SO_4 (conc.) or NaOH solution are used to adjust pH of the gel mixture to an appropriate level if it is necessary. After the addition, stir gel mixture for 1 h, and is separated from supernatant liquid by centrifuge. Secondly, a decantation solution is prepared by adding solution A2 and solution B2 into solution C2, same as for the preparation of gel mixture. The supernatant liquids from A2, B2 and C2 are mixed together with the gel mixture. However, before mixing, the pH of solution is maintained between 9-11. The colorless supernatant liquid is separated from the mixture by centrifugation.

3.1.2.2 Crystallization

The mixture of the milling precipitate and the supernatant of decant solution is filled in a 500 ml pyrex glass. The glass container is placed in a stainless steel autoclave. The atmosphere in the autoclave is replaced by nitrogen gas and pressurized up to 3 kg/cm^2 gauge. Then, the autoclave is heated from room temperature to 180 ^oC and keeps at this temperature for 3 days, follow by cooling the mixture to room temperature in the autoclave overnight. The product crystals are washed with de-ionized water by centrifugation in order to remove chloride out of the crystals. Then the crystals are dried in an oven at 110 ^oC for at least 24 h.

3.1.2.3 Calcination

The dry crystals are calcined in an air stream at 550 ^{o}C and held at that temperature for 7 h, by heating them from room temperature to 550 ^{o}C at a heating rate 8.6 ^{o}C/min, to burn off the organic template leave the cavities and channels in the crystals. Then, the calcined crystals are finally cooled down to room temperature in a desiccator.

3.1.3 Treatment catalysts

10 g of Co-TS-1 or TS-1 is placed in a round bottom flask and then 150 ml of 5M HNO_3 aqueous solution is added. After reflux at 80 °C for 3 h, the pretreated catalyst is filtered, washed with distilled water until pH 7, dried at 110°C and calcined at 540 °C for 7 h in static air.

3.2 Catalyst characterization

3.2.1 X-Ray Fluorescence Spectrometer (XRF)

The chemical composition analysis of elements of the catalyst is performed by X-ray fluorescence (XRF) using Siemens SRS3400.

3.2.2 BET surface area measurement

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

3.2.3 X-Ray Diffraction (XRD)

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

3.2.4 Fourier transform Infrared (FT-IR)

The functional group on the catalyst surface is determined by FT-IR using Nicolet model Impact 400. Infrared spectra are recorded between 400 and 1300 cm^{-1} on a microcomputer

3.2.5 NH_3 Temperature programmed desorption (NH_3-TPD)

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

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

3.3 Reaction study in the hydroxylation of toluene

3.3.1 Reaction procedure

The hydroxylation of toluene with H_2O_2 (30 wt% in water, Merck) is carried out in a 250 ml, paraffin oil jacketed, three-necked, glass flask fitted with a condenser and a mechanical stirrer place in a stirring block heater, see **Figure 3.2.** The reaction is performed at atmospheric pressure. Typically, 1 g of a catalyst is reacted with toluene and H_2O_2 at a molar ratio equals to 1 to 1 with 50 ml of water which acts as solvent. If x ml of 0.l M acid is added, the volume of water used will be reduced to 50-x ml. First, the catalyst and water using for dispersion of a catalyst are added into a reactor at 90 °C for 1 hour so as to drive out gases in pores of catalyst. Then 1 ml of toluene is added into the reactor. 1 ml of H_2O_2 is slowly injection dropwise (0.1 ml per 12 min) into the reactor. The overall reaction time (counts from the first drop of H_2O_2 is added) in 2 hours. The reaction has been stopped by cooling down, the reactor in an ice bath, after that 50 ml of ethanol is added into reactor to homogenize the aqueous phase and the organic phase. The reaction products are analyzed by a gas chromatograph equipped with a FID detector (SHIMADZU GC9A). Operations condition of the gas chromatograph is listed in **Table 3.3**.

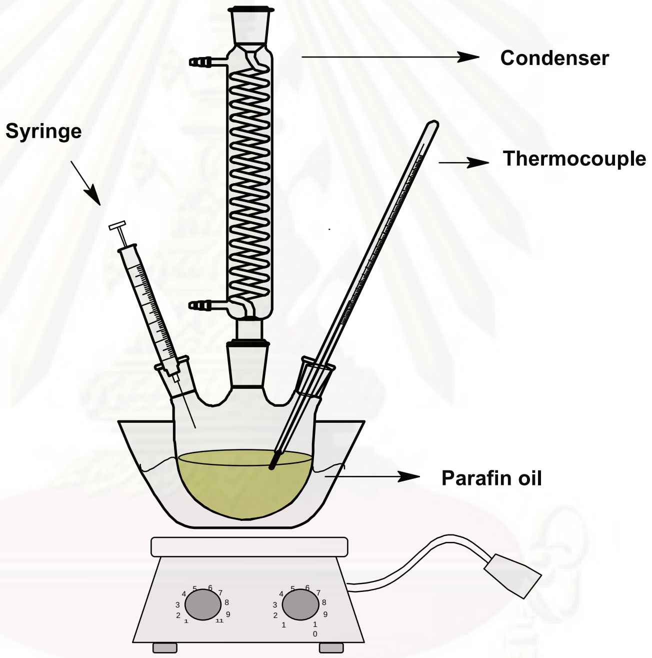


Figure 3.2 The hydroxylation reactor

Table 3.3 Operating conditions for gas chromatograph

Gas chromatograph	SHIMADZU GC9A
Detector	FID
Packed column	GP 10% SP-2100
Carrier gas	N_2 (99.999%)
Carrier gas flow rate (ml/min)	30
Injector temperature (°C)	250
Detector temperature (°C)	250
Initial column temperature (°C)	80
Initial hold time (min)	5
Program rate (°C/min)	2
Final column temperature (°C)	230
Analyzed chemicals	Toluene, Benzaldehyde and cresol

3.3.2 Calculation of %H_2O_2 converts to product, productivity and %selectivity

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

1. The percentage of H_2O_2 converts to product

$$\%\,\mathrm{H_2O_2}\ \text{convert to product} = \frac{(2\times \text{mole of benzaldehyde}) + \text{mole of cresol}}{\text{mole of } \mathrm{H_2O_2}} \times 100$$

2. The productivity of benzaldehyde (µmol/min·g)

$$\text{Productivity of benzaldehyde} = \frac{\text{mole of benzaldehyde}}{\text{weight catalyst (g)} \times 120\ \text{min} \times 10^{-6}}$$

For the productivity of o-cresol and p-cresol can calculate by apply the equation of productivity of benzaldehyde but the mole of o-cresol and p-cresol is used instead of the mole of benzaldehyde.

3. The %selectivity of benzaldehyde

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

For the %selectivity of o-cresol and p-cresol can calculate by apply the equation of %selectivity of benzaldehyde but the mole of o-cresol and p-cresol is used instead of the mole of benzaldehyde.

CHAPTER IV

RESULTS AND DISCUSSION

The results and discussion in this chapter is divided in two sections: (1) characterization of catalysts and (2) catalytic performance evaluation. The physical characterization comprises of XRF to measure the catalyst compositions, XRD to identify crystal structure, FT-IR to indicate the location of titanium cation, BET to measure the surface area, and NH_3-TPD to determine the strength and amount of acid site of the catalysts. These properties are reported in section 4.1. The catalytic activity of TS-1 and TS-1 modified with Co (Co-TS-1) in the reaction between toluene and hydrogen peroxide are reported in section 4.2.

4.1 Catalyst characterization

4.1.1 Chemical compositions

The chemical compositions of TS-1 and Co-TS-1 are determined by X-Ray Fluorescence Spectrometer (XRF). The results are exhibited in **Table 4.1**.

Table 4.1 The chemical compositions of TS-1 and Co-TS-1

samples	Si (%mol)	Ti (%mol)	Co (%mol)	Si/Ti (%mol)	Si/Co (%mol)
TS-1	97.72	1.98	none	49	none
Co-TS-1(Si/Co=50)	98.59	1.25	0.080	78	1233
Co-TS-1(Si/Co=100)	97.76	2.11	0.076	46	1292
Co-TS-1(Si/Co=150)	97.64	2.07	0.071	47	1377
Co-TS-1(Si/Co=200)	97.91	1.98	0.048	49	2050

The results in the table above show that the cobalt cation can be incorporated into the MFI structure of catalysts. The amount of cobalt in Co-TS-1 that obtained from X-Ray Fluorescence Spectrometer increases when the amount of cobalt is added into the gel and decant solutions increase. The explanation of this phenomenon is if cobalt concentration in the gel and decant solutions further increased, the chance of cobalt cations incorporate into the MFI framework during the crystallization step increase. Therefore, the final concentration of cobalt in the obtained Co-TS-1 will increase.

The amount of titanium cation that can be incorporated in the MFI structure increases proportionally with the amount of titanium that added before crystallization. On the contrary, the amount of cobalt added before crystallization and the amount of cobalt appeared in the obtained catalysts does not relate proportionally. Due to the corporation of cobalt cation into the MFI structure is in random form and the cobalt cation can form cobalt oxide which can be washed out in the treatment step. Therefore, it is very difficult to fix the ratio of Si/Co of the synthesized catalyst for each sample.

From section 4.1.2 forward, Co-TS-1(1233) represents Co-TS-1 having Si/Co = 50. In the same way, Co-TS-1(1292), Co-TS-1(1377), and Co-TS-1(2050) represent Co-TS-1 having Si/Co = 100, 150 and 200, respectively.

4.1.2 Crystal structure

The crystal structure of all prepared catalysts is identified using x-ray diffraction technique details described previously in section 3.2.3. The XRD patterns of TS-1 and TS-1 modified with Co are summarized in **Figure 4.1**. All XRD patterns show six main characteristic peaks at $2\theta \approx 8$, 8.8, 14.8, 23.1, 24 and 26.7 which are typical for MFI structure (Taramasso et al., 1983). The XRD pattern of cobalt oxide does not appeared in any obtained pattern.

The absence of the peak at $2\theta \approx 25.3$, the strongest peak of TiO_2 in anatase phase, shows that anatase does not exist in the TS-1 and Co-TS-1 which synthesized using TPABr as the template (Li et al., 2001). These XRD patterns also show that the incorporation of cobalt into TS-1 catalyst does not destroy the MFI structure of the catalyst.

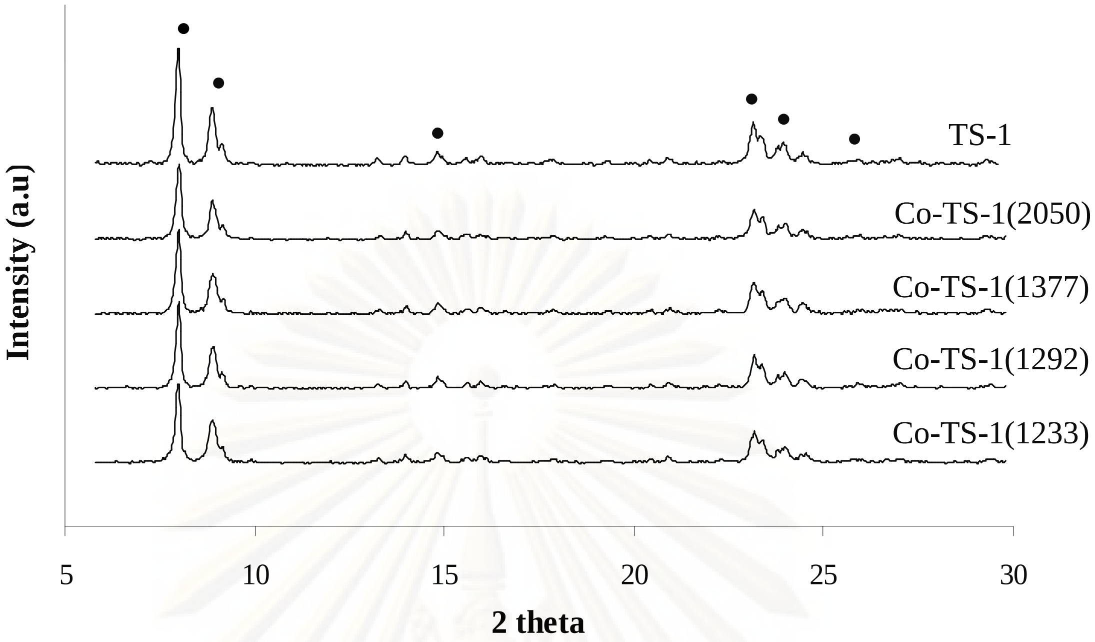


Figure 4.1 The XRD patterns of TS-1 and Co-TS-1

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

4.1.3 Location of titanium cation

The characteristic absorption band of Ti^{4+} in the TS-1 and modified TS-1 is presented in **Figure 4.2**. All samples have the absorption band at 960 cm^{-1}, having slightly different strength, which indicates that Ti^{4+} has been incorporated into the framework of TS-1 zeolite (Liu et al., 2005 and Bengoa et al., 1998). Grieneisen et al. (2000) reported that FT-IR spectra exhibited a strong absorption band at 960 cm^{-1} can be attributed to a stretching mode of an [SiO_4] unit bonded to a Ti^{4+} ion (O_3SiOTi). Some researcher suggested that the catalytic performance of TS-1 is related to the amount of Ti on the framework of zeolite (Liu et al., 2006).

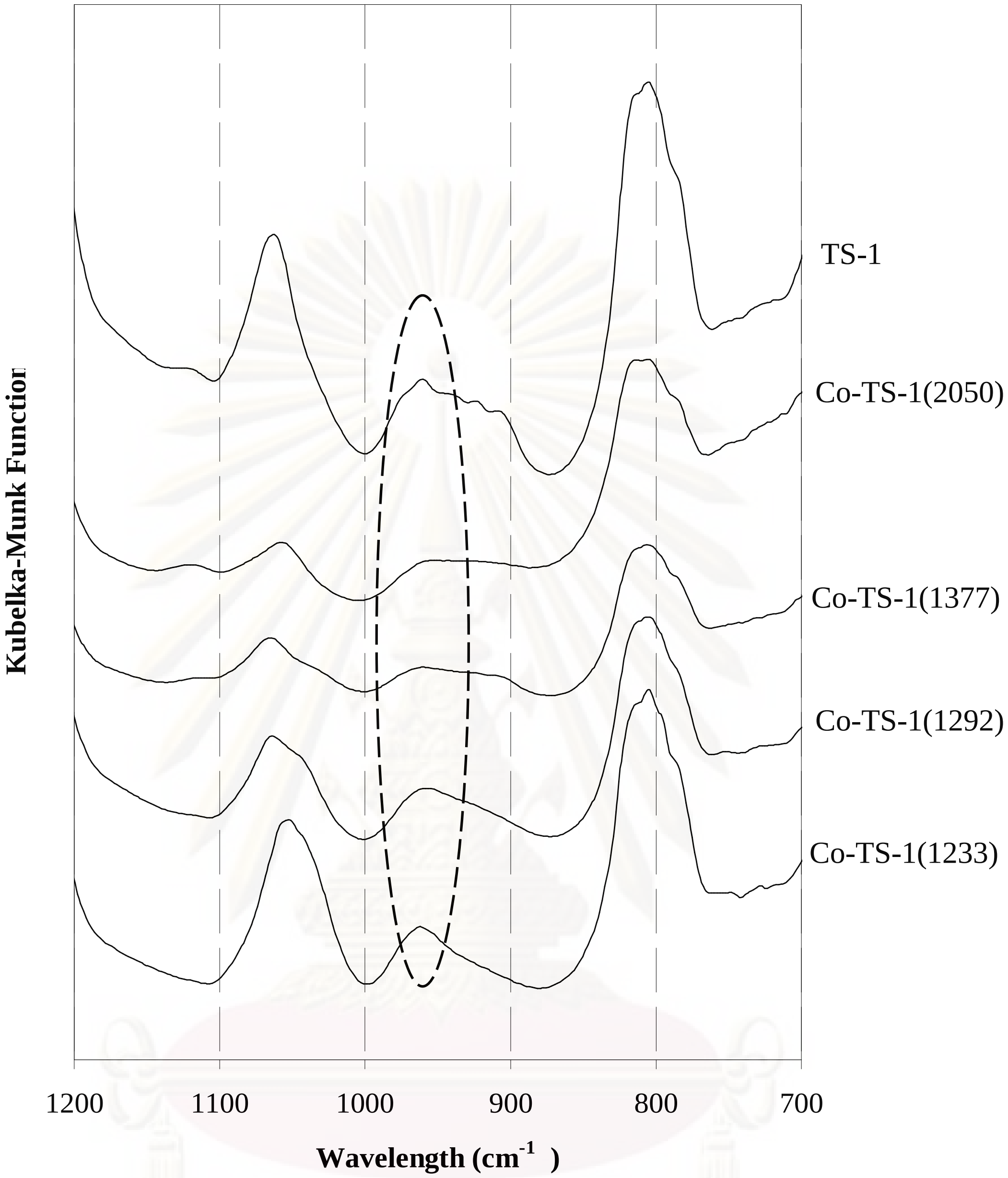


Figure 4.2 The absorption band of TS-1 and Co-TS-1 in wave number range between 700 – 1200 cm^{-1}

4.1.4 Surface Area

The surface area of TS-1 and all Co-TS-1 samples are tabulated in **Table 4.2**. All samples have surface area in the range 336-388 m^2/g which is not so different. Hence, any different 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 Co-TS-1

Sample	A_{BET} (m^2/g)
TS-1	354
Co-TS1(1233)	388
Co-TS1(1292)	350
Co-TS1(1377)	336
Co-TS1(2050)	349

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 cobalt 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 cobalt of each sample.

4.2 The catalytic performance of reaction

The catalytic performance of TS-1 and Co-TS-1 were tested with the reaction between toluene and hydrogen peroxide. This reaction produces mainly three products: benzaldehyde, ortho-cresol and para-cresol. The experimental results are reported in the form of the total percent of hydrogen peroxide converted to products and moles of each product formed. In this research, the influence of concentration of acid in solution by carries out the reaction without and with different amount of acid (HCl) in the aqueous H_2O_2 phase was investigated.

The reaction occurs in the stirred reactor. In this 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 and H_2O_2 is added into the reactor. During this period, the catalyst will contact with toluene and H_2O_2. 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 water phase which filled in the pores. In this case, the concentration of toluene depends on the solubility of toluene in water. Both phenomena are showed graphically in **Figure 4.3**

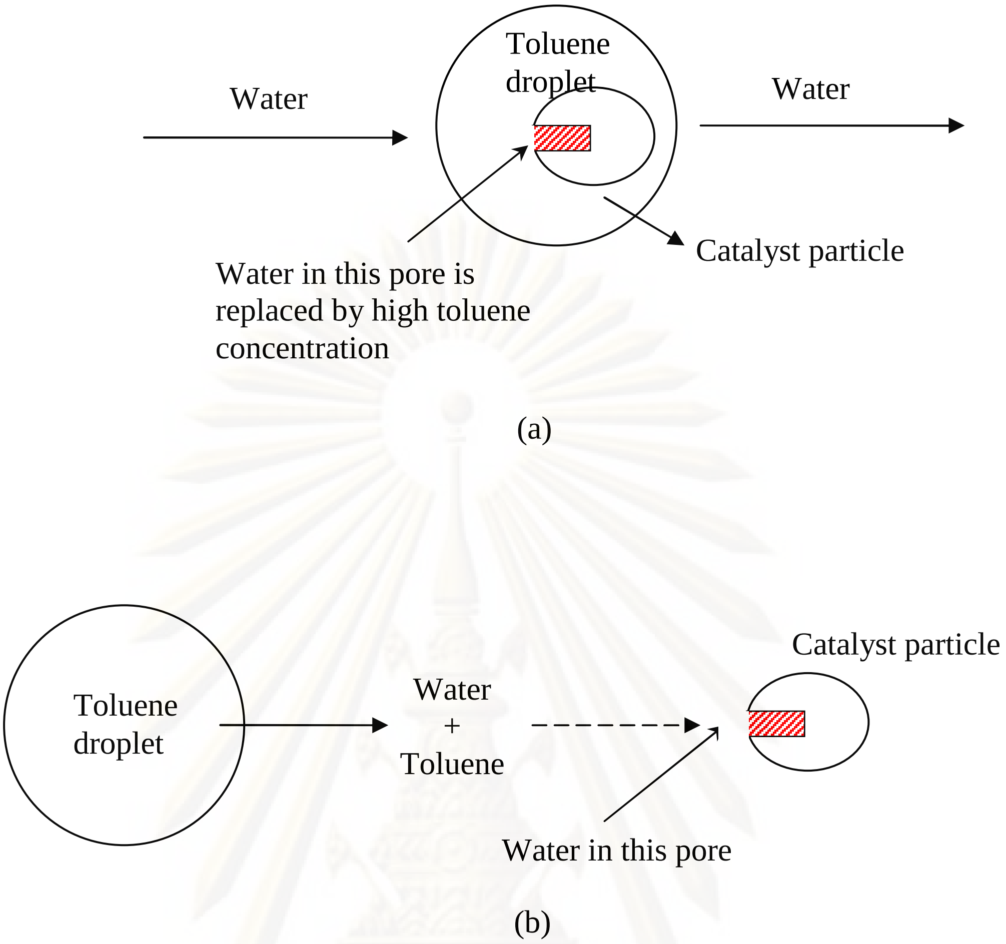


Figure 4.3 The phenomena during toluene contact with catalyst particle

(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.

4.2.1 The effect of proton

The first question has to be answered is proton (H^+) really affects the reaction. To answer this question, an experiment is set up to confirm the role of proton during the reaction. In this experimental testing, a solution of NaCl (0.1 M) is used instead of the solution of HCl (0.1 M). Other experimental procedures and parameters are the same. The only difference is the solution of NaCl is used instead of the solution of HCl.

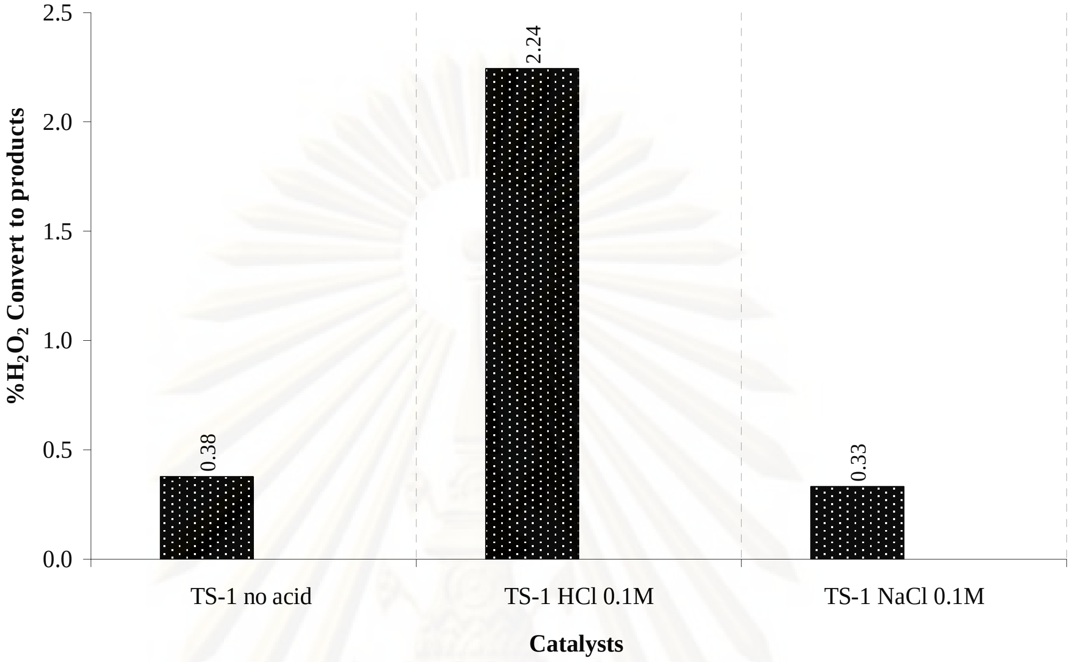


Figure 4.4 Percentage of H_2O_2 converts to product at 90 ºC

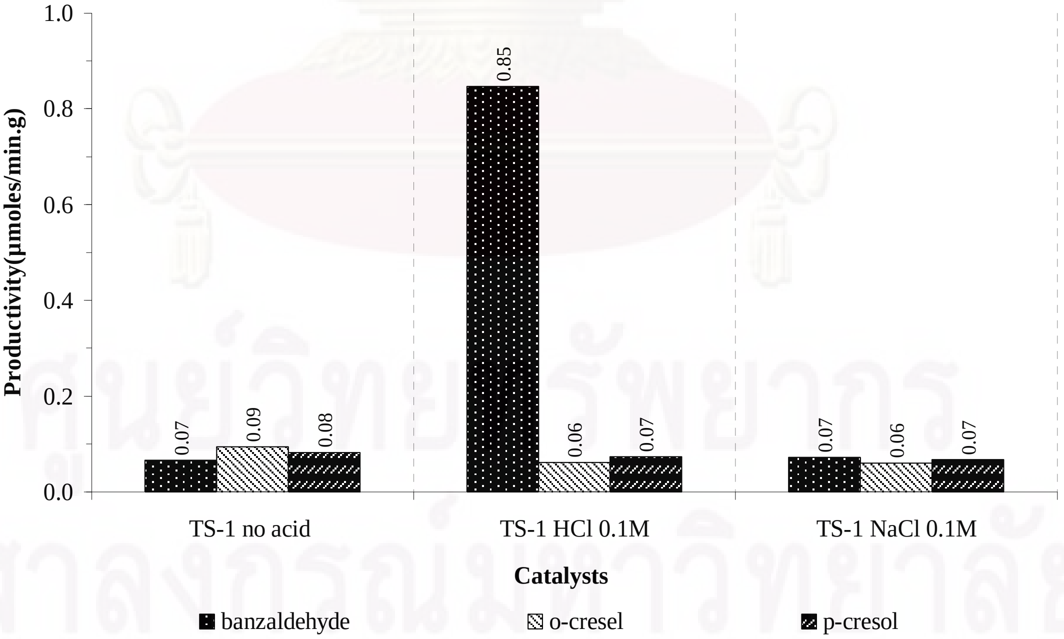


Figure 4.5 Productivity at 90 ºC

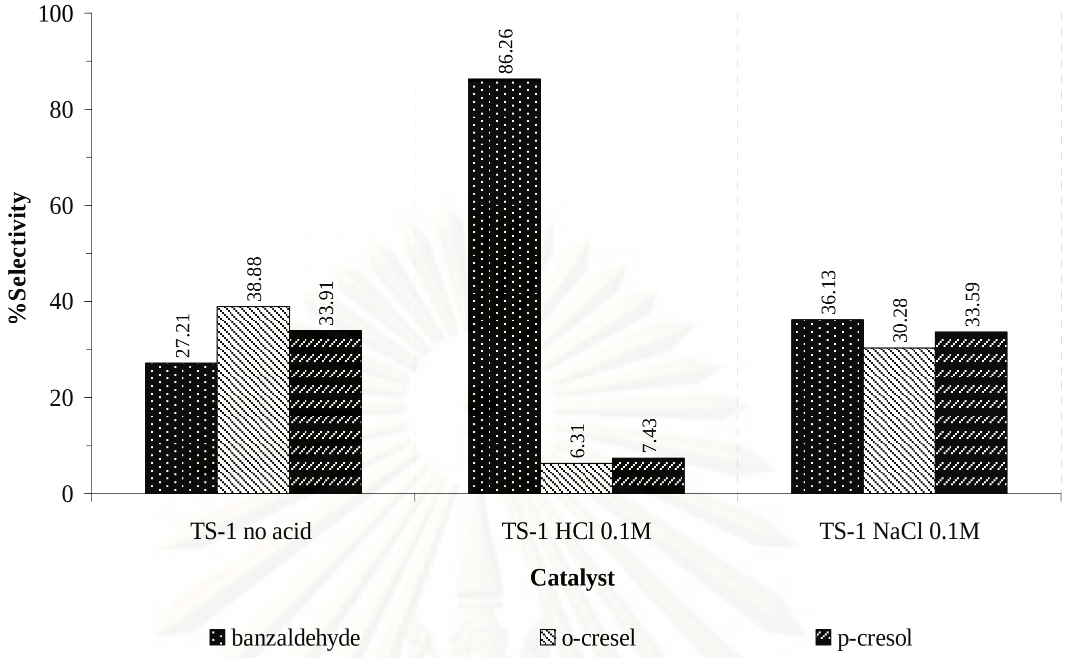


Figure 4.6 Percentage of selectivity at 90 ºC

Figures 4.4-4.6 compare the result obtained from using TS-1 catalyst. In the first experiment 50 ml of distilled water is used as solvent. In the second experiment 40 ml of water plus 10 ml of 0.1 M HCl is used as solvent. In the third experiment 40 ml of water and 10 ml of 0.1 M NaCl is used as solvent. One can clearly seen from the experimental results that only when HCl is presented in the solution, the catalytic activity (the conversion of H_2O_2) of the catalyst change dramatically. From this evidence, it can be concluded that proton (H^+), not the anion (Cl^-), does really play a major role on the enhancing catalytic activity of the catalyst.

4.2.2 The effect of acidity of solution in each catalyst

The parameter affecting the reaction to be discussed is the effect of acidity of solution (without and with hydrochloric acid 0.1M 10 ml) on the performance of each catalyst. The effect of acidity of solution on the percentage of H_2O_2 converted to products, productivity and selectivity obtained at the reaction temperature 70°C are illustrated in **Figures 4.7-4.9**. **Figure 4.7** shows the percentage of H_2O_2 converted to products, **Figure 4.8** shows the productivity and **Figure 4.9** shows the selectivity.

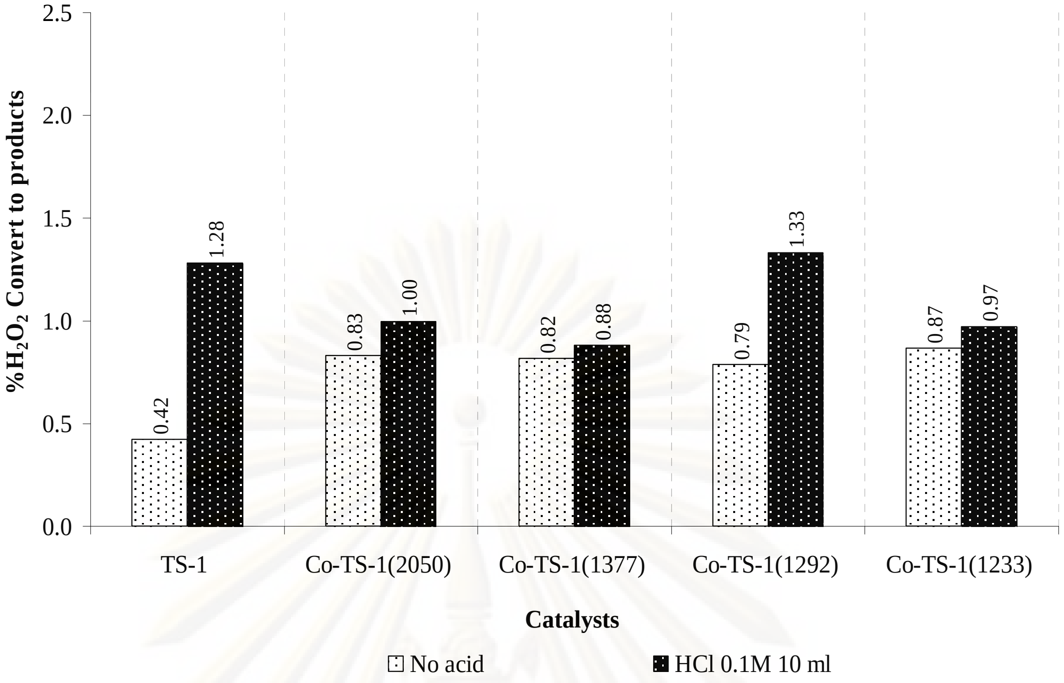


Figure 4.7 Percentage of H_2O_2 converts to product at 70 ºC

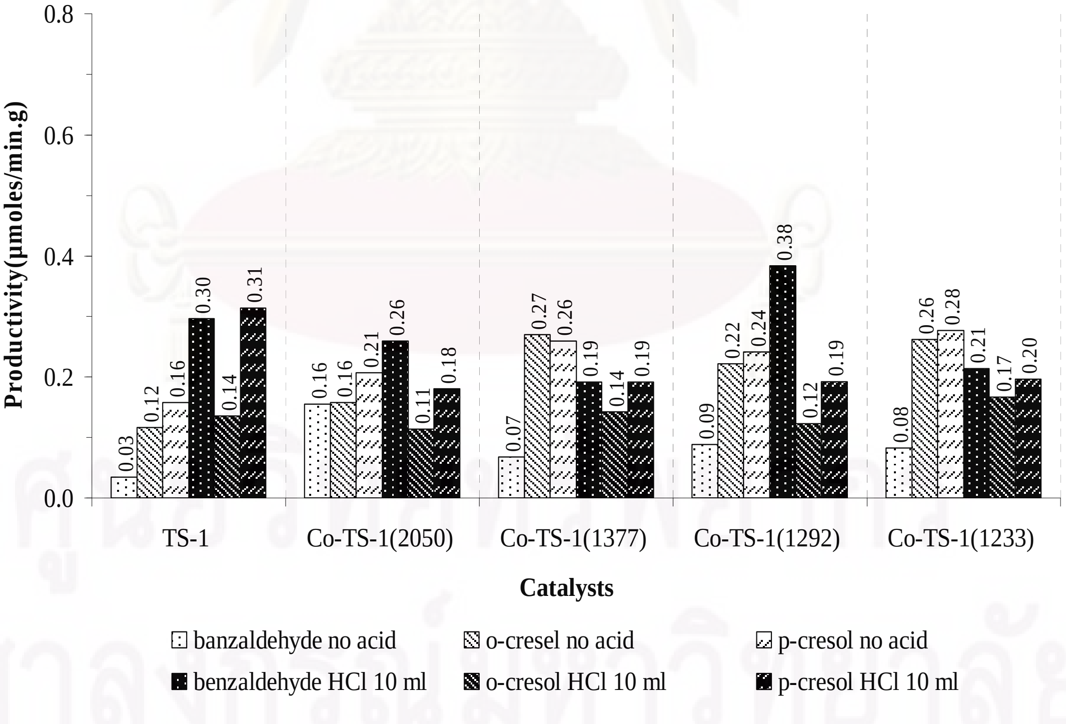


Figure 4.8 Productivity at 70 ºC

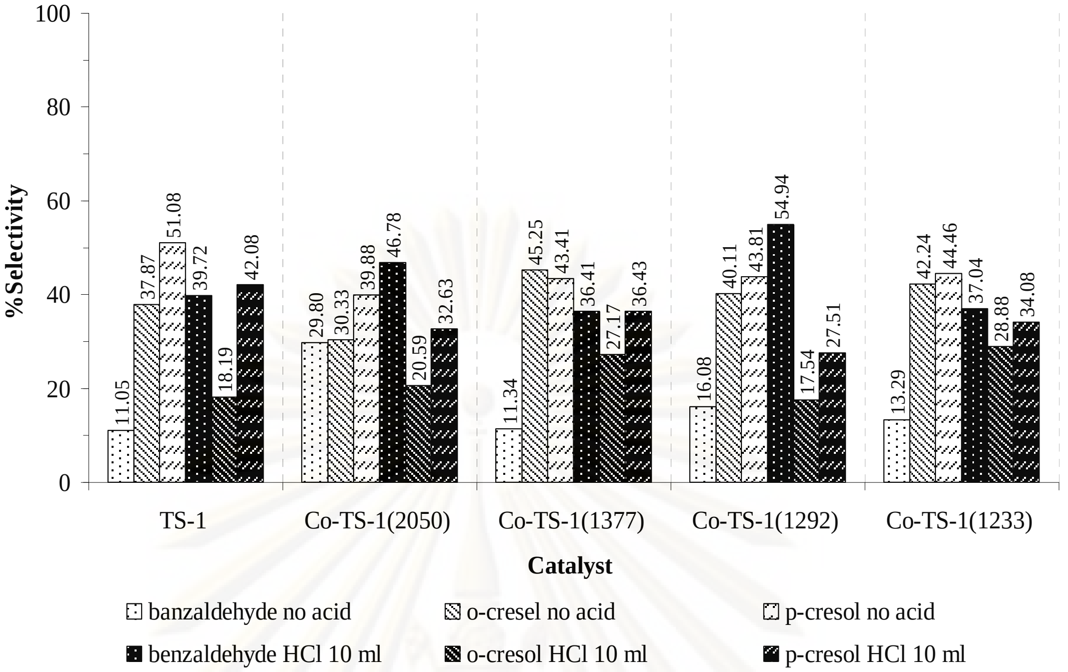


Figure 4.9 Percentage of selectivity at 70 ºC

Figure 4.7 shows the percentage of H_2O_2 conversion for reaction with and without acid at reaction temperature 70 °C. The catalyst TS-1 has the lowest percentage of H_2O_2 conversion among all catalysts studied without acid in the aqueous solution. The reason of this result may relate to the amount of active site. When the solution is added with hydrochloric acid, the percentage of H_2O_2 conversion is higher for all catalysts. Especially, TS-1 and Co-TS-1(1292) which show the extremely enhance of percentage of H_2O_2 conversion. The percentage of H_2O_2 conversion increases from 0.42 to 1.28 which is about 305% for TS-1 and increases from 0.79 to 1.33 which is about 168% for Co-TS-1(1292).

The productivities of organic products (benzaldehyde, o-cresol, and p-cresol) of each catalyst are showed in **Figure 4.8**. In the reaction without acid, the production of both o-cresol and p-cresol is higher than benzaldehyde for all the catalysts. But when the solution is added with hydrochloric acid, the benzaldehyde production increase and the cresol production decreases. Therefore, the acidity of the solution promotes benzaldehyde production in this reaction.

The effect of acidity of solution on the percentage of H_2O_2 converted to products obtained at the reaction temperature 90°C are illustrated in **Figures 4.10-4.12**. **Figure 4.10** shows the percentage of H_2O_2 converted to products, **Figure 4.11** shows the productivity and **Figure 4.12** shows the selectivity.

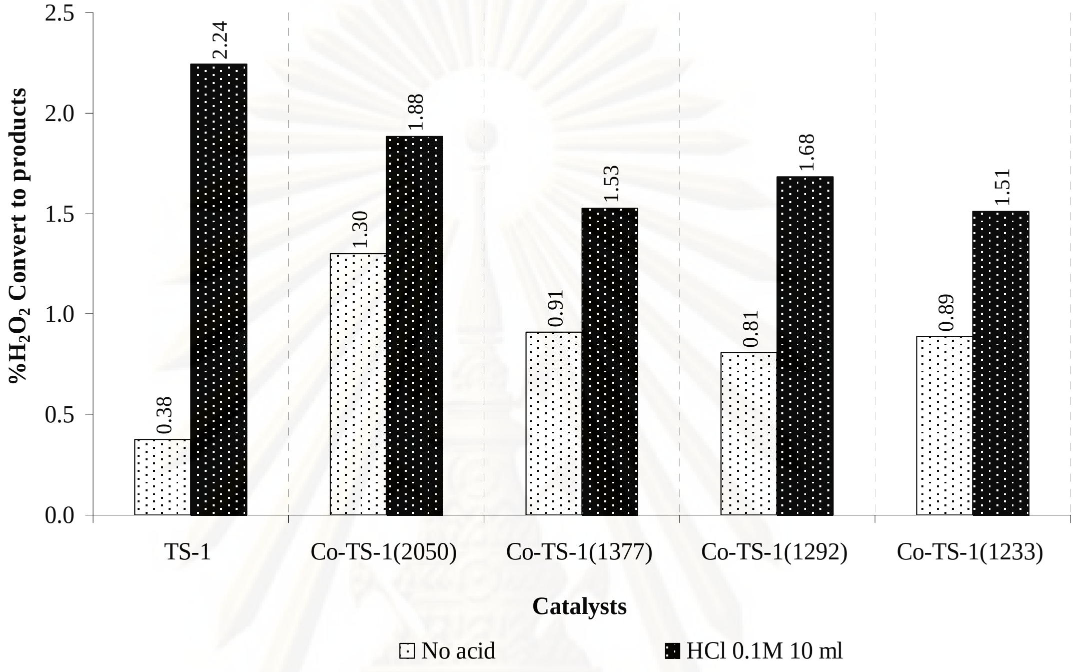


Figure 4.10 Percentage of H_2O_2 converts to product at 90 °C

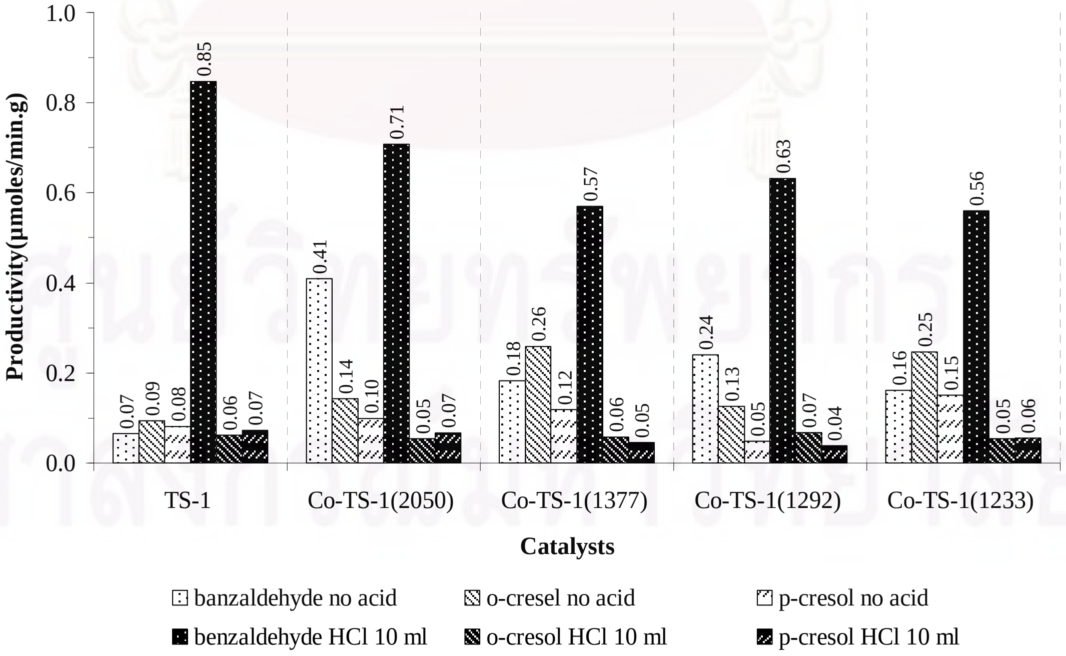


Figure 4.11 Productivity at 90ºC

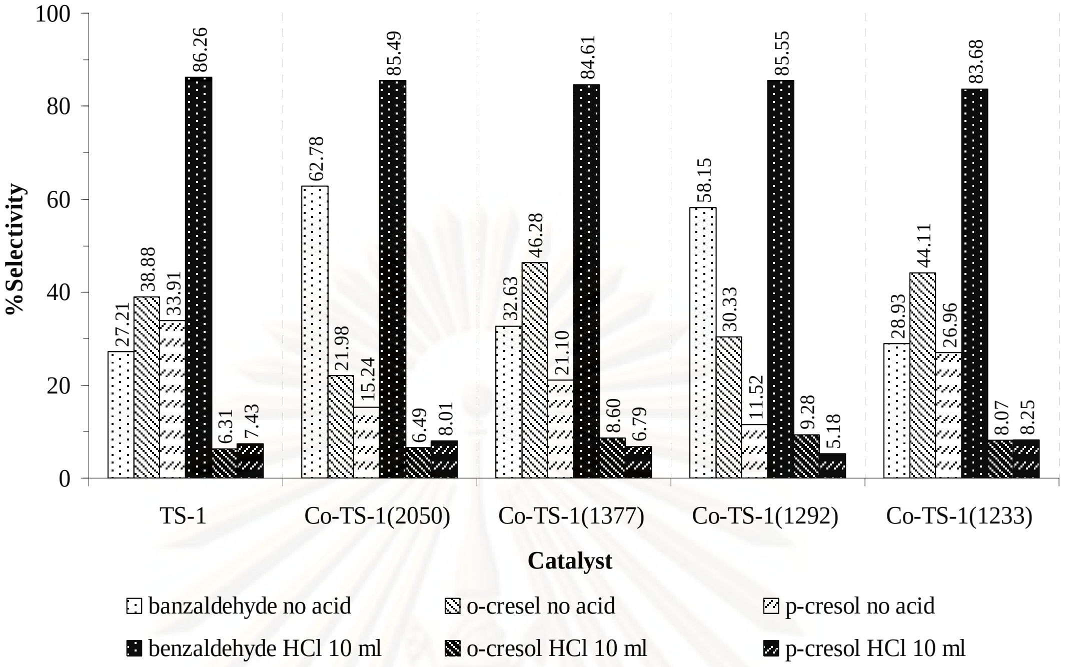


Figure 4.12 Percentage of selectivity at 90ºC

Figure 4.10 shows the percentage of H_2O_2 conversion for reaction with and without acid at reaction temperature 90 °C. The catalyst TS-1 has the lowest percentage of H_2O_2 conversion and the catalyst Co-TS-1(2050) has the highest percentage of H_2O_2 conversion among for all the catalysts studied without acid in the aqueous solution. The reason of this result may relate amount of active site. When the solution is added with hydrochloric acid, the percentage of H_2O_2 conversion is higher for all the catalysts. Especially, TS-1 and Co-TS-1(1292) which show the extremely enhance of percentage of H_2O_2 conversion in reaction. The percentage of H_2O_2 conversion increases from 0.38 to 2.24 which is about 590% for TS-1 and increases from 0.81 to 1.68 which is about 208% for Co-TS-1(1292).

The productivities of organic products (benzaldehyde, o-cresol, and p-cresol) of each catalyst are showed in **Figure 4.11**. The benzaldehyde production very increase and the cresol production slightly decrease in solution is added hydrochloric acid. Therefore, the acidity of solution promotes benzaldehyde production at this reaction temperature also.

4.2.3 The effect of temperature.

When the reaction temperature increases the following phenomena will occur:

a) The reaction rate constant will increase following the Arrenius's equation
b) The concentration of toluene in the pore of the catalyst will increase follow reaction temperature.

The hydroxylation of toluene requires the existence of two reactant molecules (toluene and H_2O_2) on the catalyst surface. 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.

The effect of reaction temperature on the percentage of H_2O_2 converted to products, productivity and selectivity obtained at the reaction without acid are illustrated in **Figures 4.13-4.15**. **Figure 4.13** shows the percentage of H_2O_2 converted to products, **Figure 4.14** shows the productivity and **Figure 4.15** shows the selectivity.

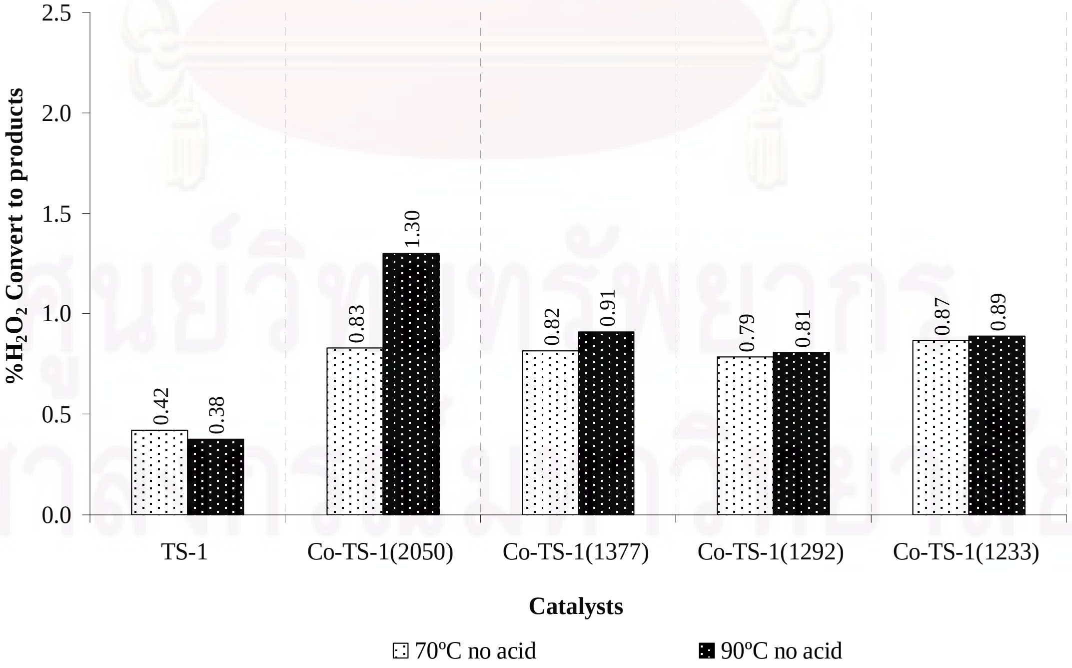


Figure 4.13 Percentage of H_2O_2 converts to product without hydrochloric acid

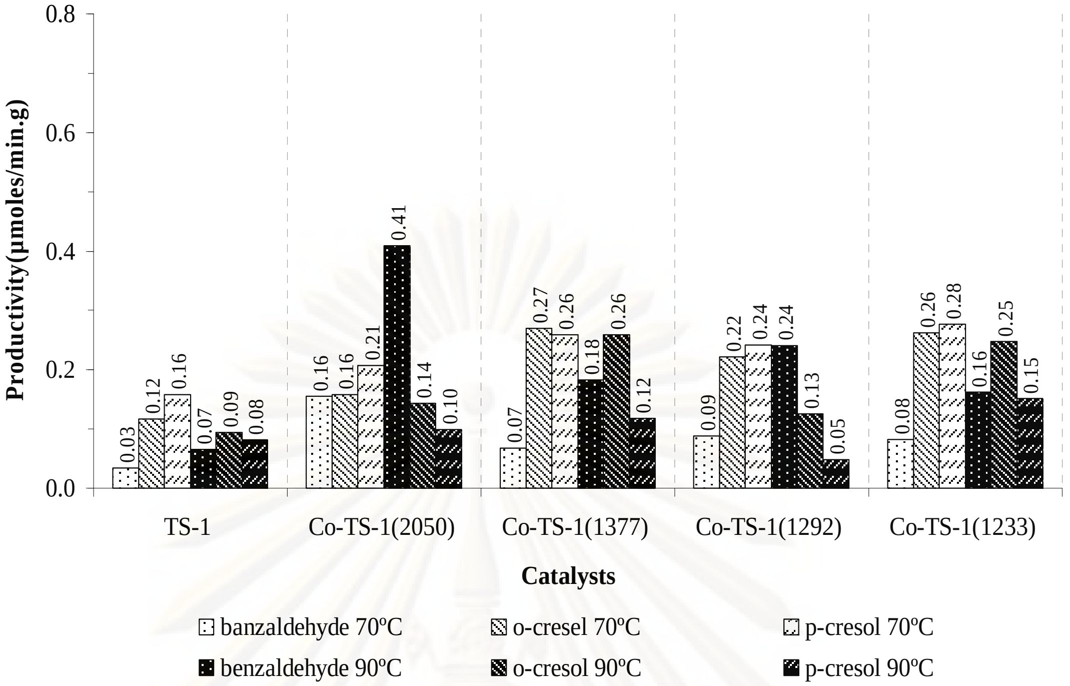


Figure 4.14 Productivity without hydrochloric acid

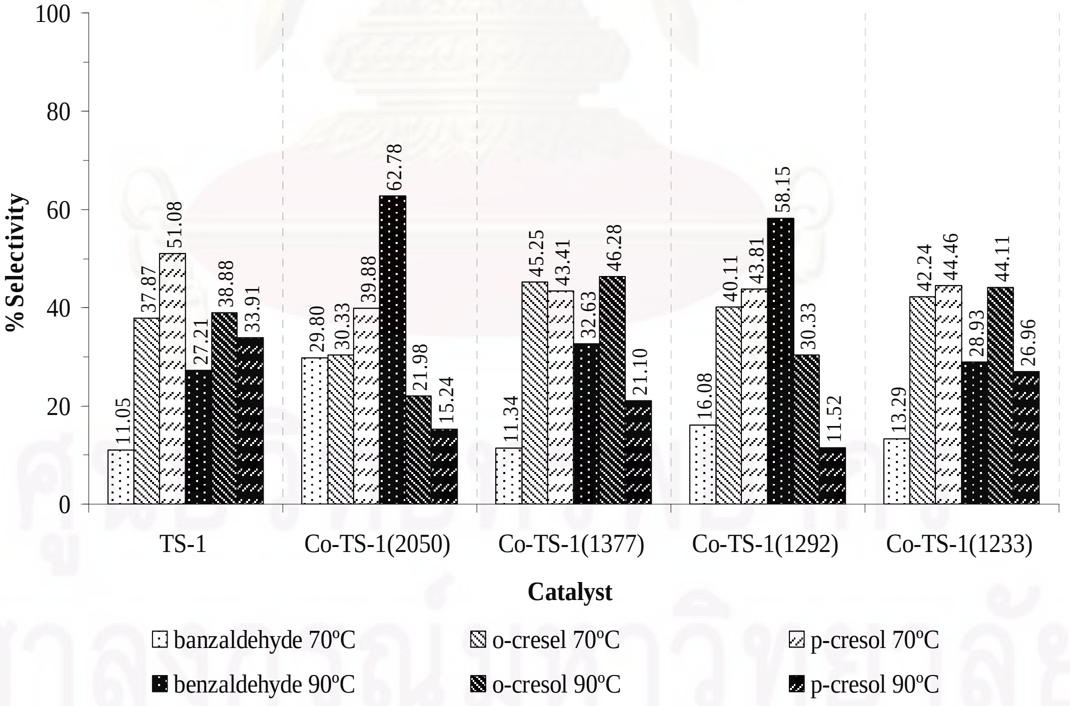


Figure 4.15 Percentage of selectivity without hydrochloric acid

The effect of reaction temperature on the percentage of H_2O_2 converted to products, productivity and selectivity obtained at the reaction with acid (hydrochloric 0.1M 10 ml) are illustrated in **Figures 4.16-4.18**. **Figure 4.16** shows the percentage of H_2O_2 converted to products, **Figure 4.17** shows the productivity and **Figure 4.18** shows the selectivity.

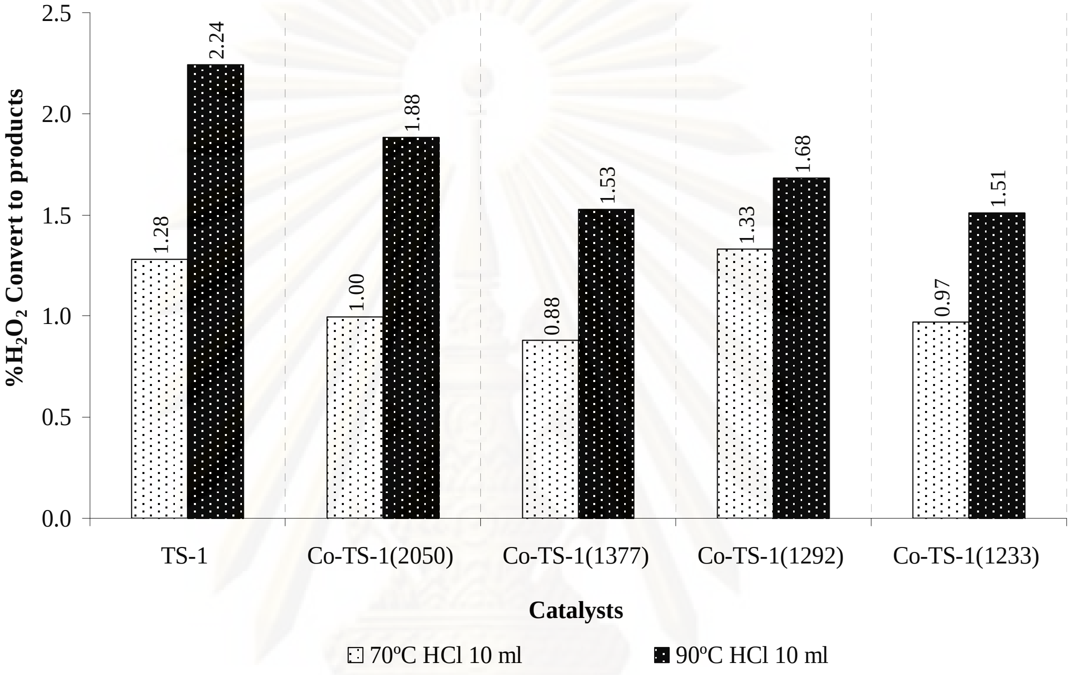


Figure 4.16 Percentage of H_2O_2 converts to product with hydrochloric acid

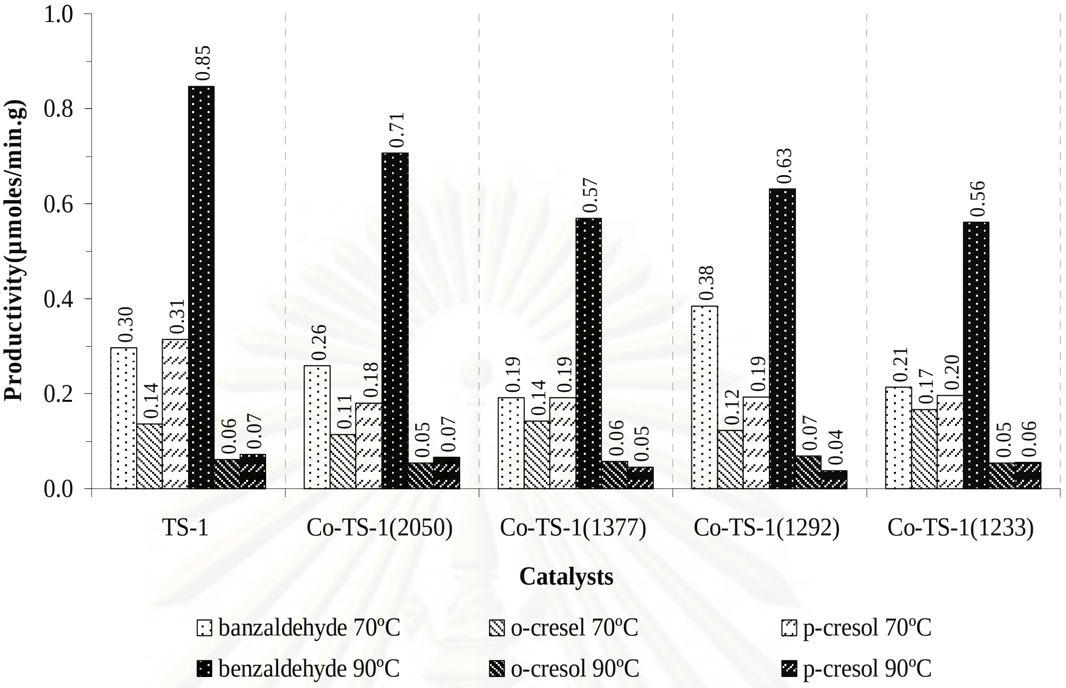


Figure 4.17 Productivity with hydrochloric acid

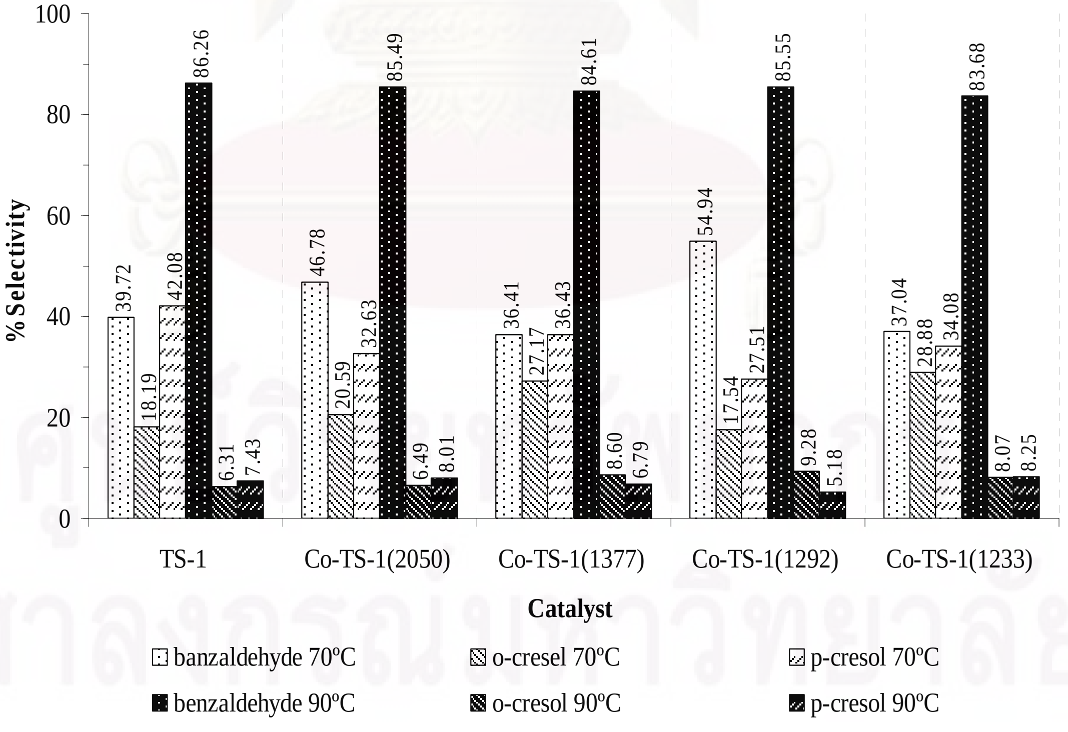


Figure 4.18 Percentage of selectivity without hydrochloric acid

At the same amount of toluene and H_2O_2, both reaction with and without acid in solution it is observed that when the reaction temperature is increased from 70 ºC to 90 ºC, the percentage of H_2O_2 converts to products are increase for all catalyst. The results are illustrated in **Figures 4.13 and 4.16**. The result is due to the phenomena that are explained above.

4.2.4 The effect of amount of acid

As illustrated in section 4.2.3, the reaction at temperature 90 ºC has the H_2O_2 conversion higher than the reaction at temperature 70 ºC. Hence, the study of the effect of amount of acid is carried out at the reaction temperature 90 ºC. The catalysts chosen for the test reaction are TS-1 and Co-TS-1(1377) that have the highest and the lowest conversion. It is possible that the conversions of catalyst that has highest conversion in reaction with hydrochloric acid 10 ml may be increase, decrease or not change with the increase of amount of acid.

The effect of amount of acid on the percentage of H_2O_2 converted to products, productivity and selectivity obtained at the reaction temperature 90 ºC for TS-1 catalyst are illustrated in **Figures 4.19-4.21**.

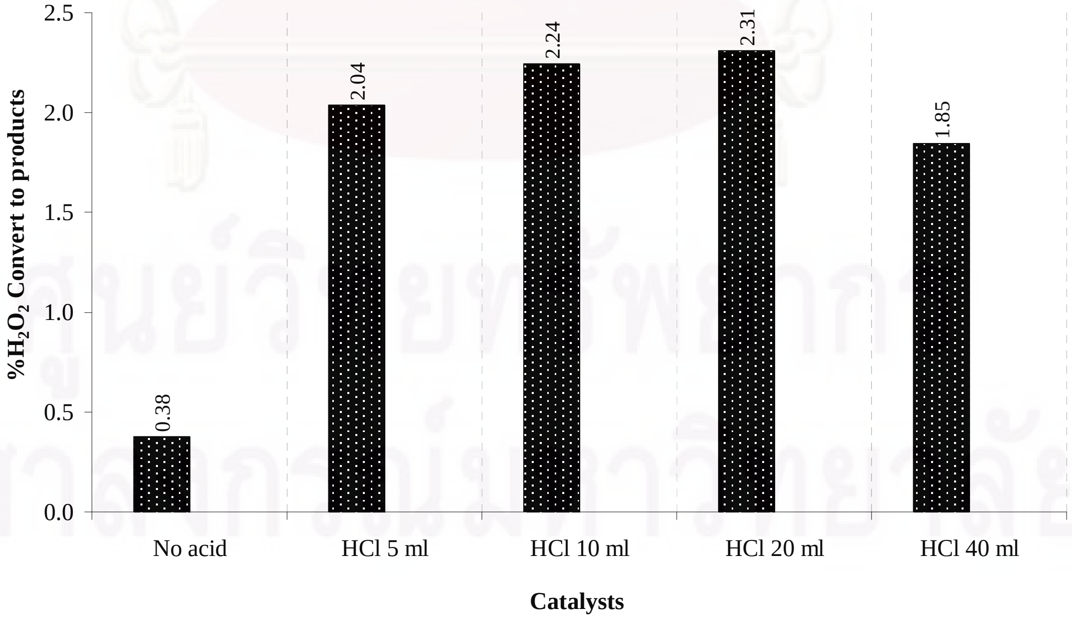


Figure 4.19 Percentage of H_2O_2 converts to product of TS-1

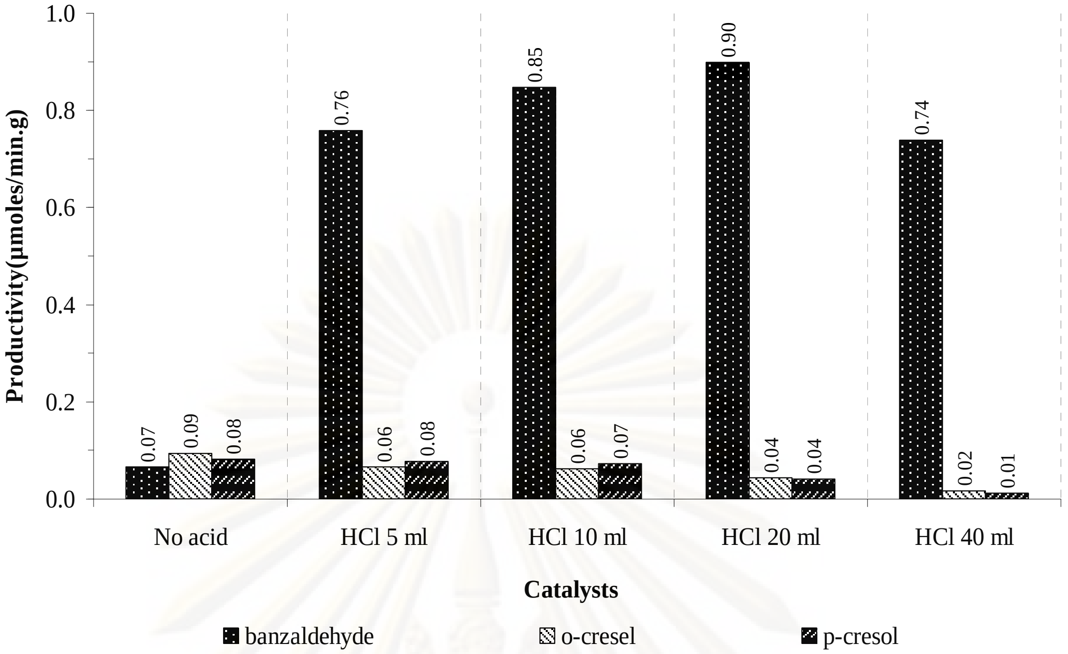


Figure 4.20 Productivity of TS-1

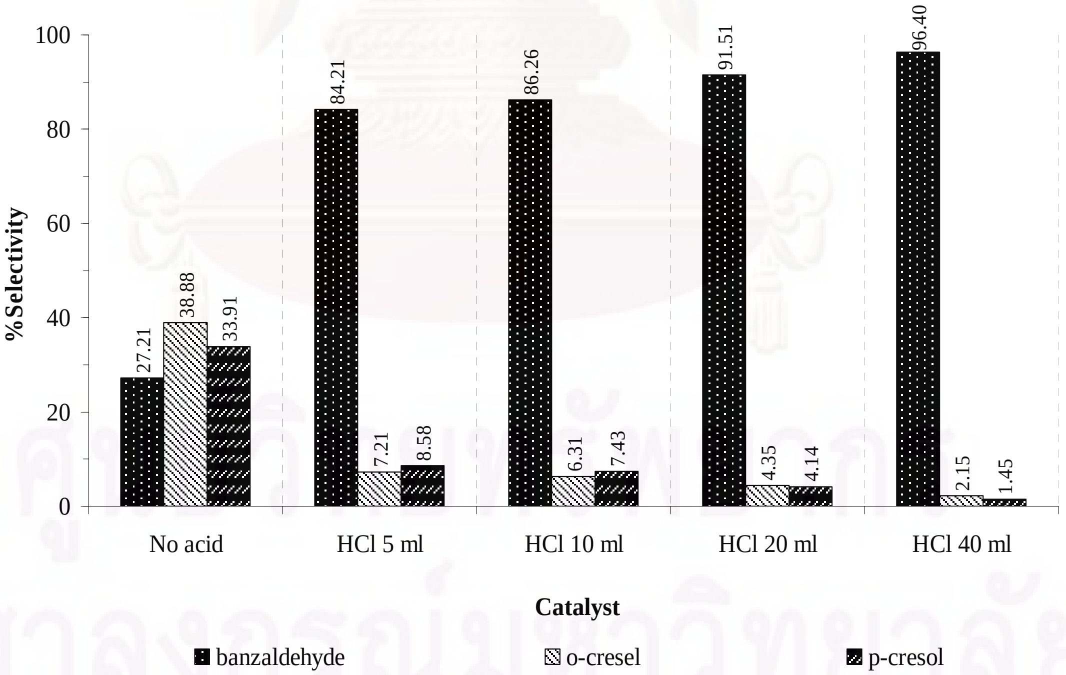


Figure 4.21 Percentage of selectivity of TS-1

The effect of amount of acid on the percentage of H_2O_2 converted to products, productivity and selectivity obtained at the reaction temperature 90 °C for Co-TS-1 (1377) catalyst are illustrated in **Figures 4.22-4.24**.

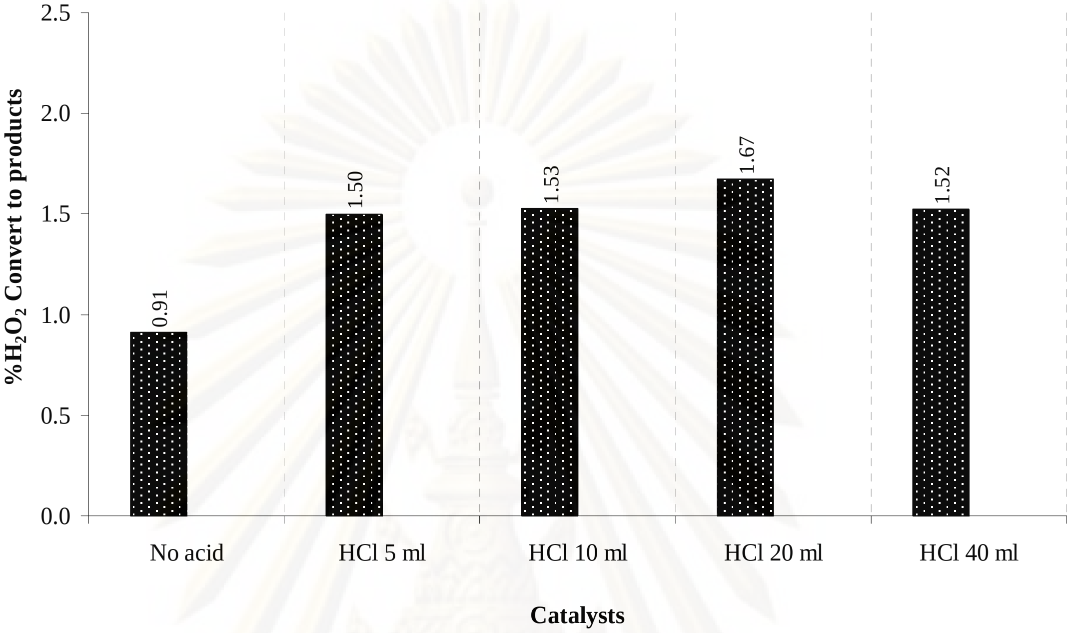


Figure 4.22 Percentage of H_2O_2 converts to product of Co-TS-1(1377)

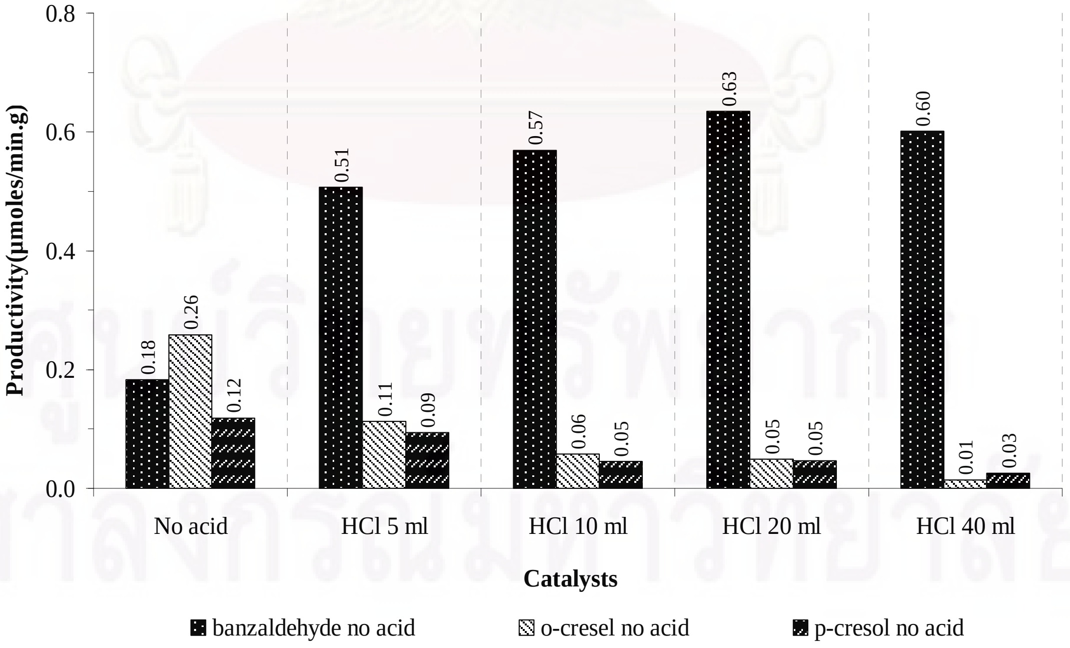


Figure 4.23 Productivity of Co-TS-1(1377)

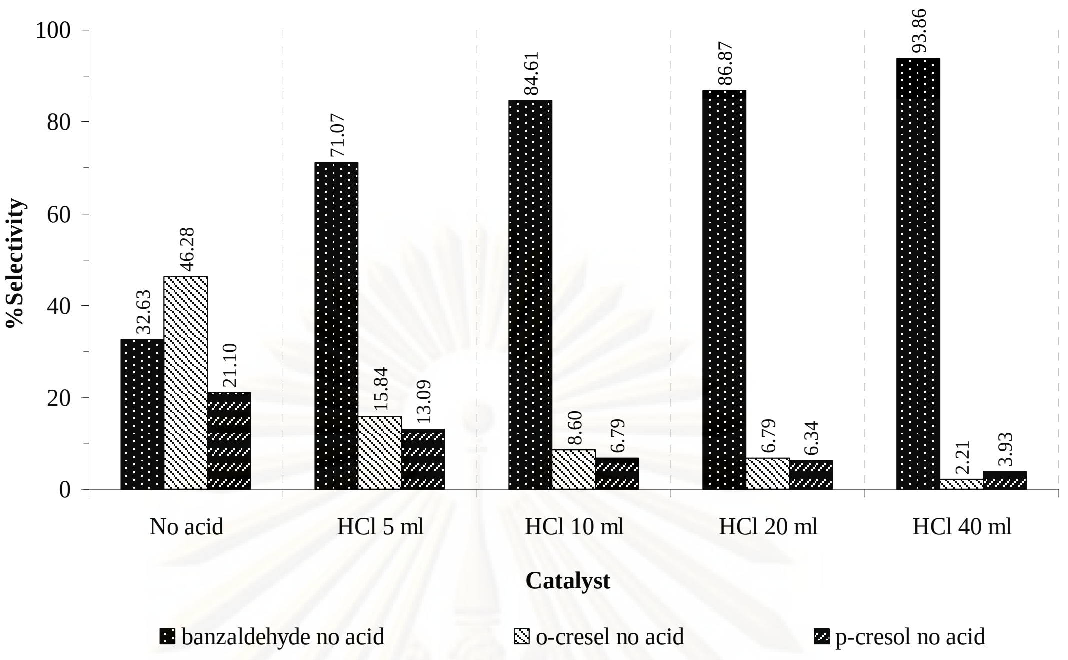


Figure 4.24 of selectivity of Co-TS-1(1377)

Figures 4.19 and **4.22** show that at a reaction temperature, the H_2O_2 conversion will depend on the amount of hydrochloric acid. The amount of hydrochloric acid increase with the H_2O_2 conversion until the amount of hydrochloric acid is 20 ml that is the maximum H_2O_2 conversion, then the H_2O_2 conversion decrease. The TS-1 catalyst still has H_2O_2 conversion higher than Co-TS-1(1377) and give benzaldehyde is the main product.

The productivity in **Figure 4.20**, for TS-1, shows that adding 0.1 M HCl up to 10 ml (while keeping the total volume of solvent at 50 ml) does not affect the formation of cresols, but significantly promotes the formation of benzaldehyde. Further increase the amount of 0.1 M HCl solution added results in the inhibition of cresol formation while the formation of benzaldehyde increases marginally. Further increase the volume of acid solution added results in the suppression of the formation of both benzaldehyde and cresol. But the formation of cresol in more strongly suppressed as can be seen from the selectivity of cresol drops clearly.

For Co-TS-1(1377) the effect of acidity on the formation of benzaldehyde and cresol can be clearly seen when only 5 ml of 0.1 M HCl is added. The productivity of benzaldehyde is greatly enhanced while the productivity of cresols drops clearly. This suggests that the presence of H^+ promotes the formation of benzaldehyde but suppresses the formation of cresol. The effect also depends on the cation i.e. the formation of cresol on Co cation is severely affected by the presence of H_3O^+ more than Ti cation.

4.3 The importance of second metal

As illustrated in section 4.1.1 that the difference among the catalysts is the amount of cobalt cation incorporated. 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 cobalt causes difference catalytic behavior.

It is generally known that titanium and cobalt cation incorporated in the silicalite framework will act as an acid site. The acidic strength inversely proportion to the amount of cobalt 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 4.25 - 4.29**.

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

The results obtained from the programmed suggest that the acidic site can categorized into 2 groups, according to their desorption peaks. The first one locates around 150-200°C which will be named here “the weak acid site” and the second one locates higher than 200 °C which will be named here “the strong acid site”. The location of each peak and amount of peak type of the acidic site are summarized in **Table 4.3**.

Even though the amount of acid site can be interpreted as the amount of cobalt and titanium cation available for the reaction, the relationship between the activities of each catalyst and the amount of available cobalt and titanium cation still can not be identified. Therefore, the activity of each catalyst does not depend on the total amount of cobalt and titanium cation available for the reaction. It also depends on the nature of the cation which will be discussed later in the next section, section 4.4.

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

Catalyst	Total acid site (μmol/g)	Weak acid strength		Strong acid strength	
		Temp. (°C)	Acid site (μmol/g)	Temp. (°C)	Acid site (μmol/g)
TS-1	53.35	190	47.48	343	5.88
Co-TS-1(2050)	183.16	164	109.55	246	73.61
Co-TS-1(1377)	114.35	168	71.93	253	42.42
Co-TS-1(1292)	124.93	161	82.43	233	42.50
Co-TS-1(1233)	85.97	174	64.95	338	21.02

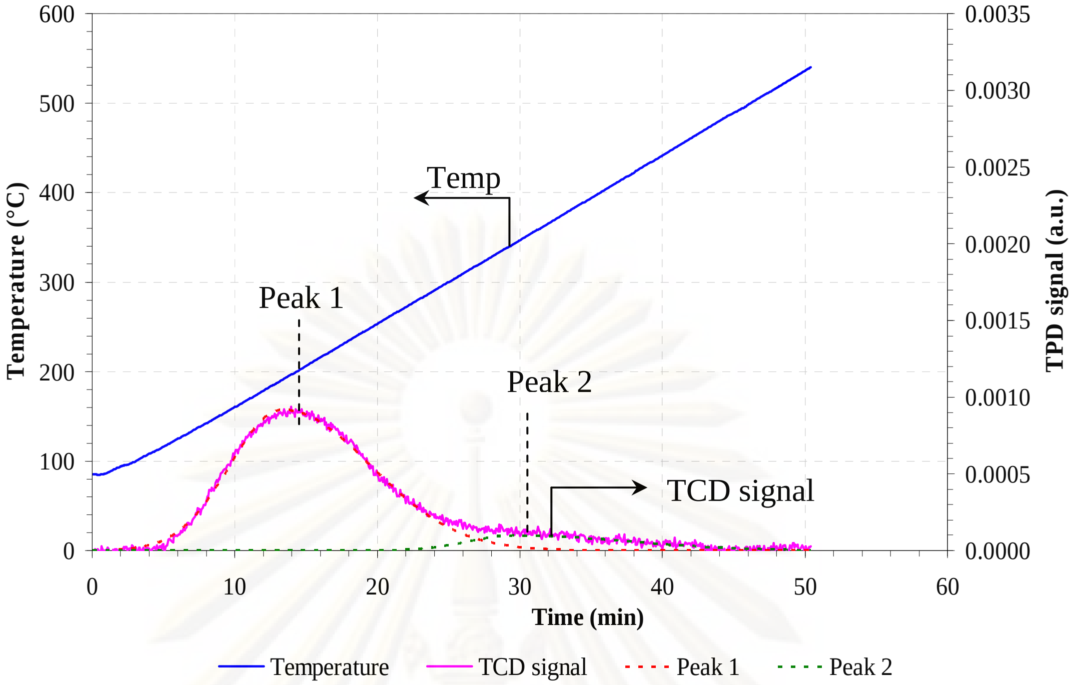


Figure 4.25 NH_3-TPD of TS-1

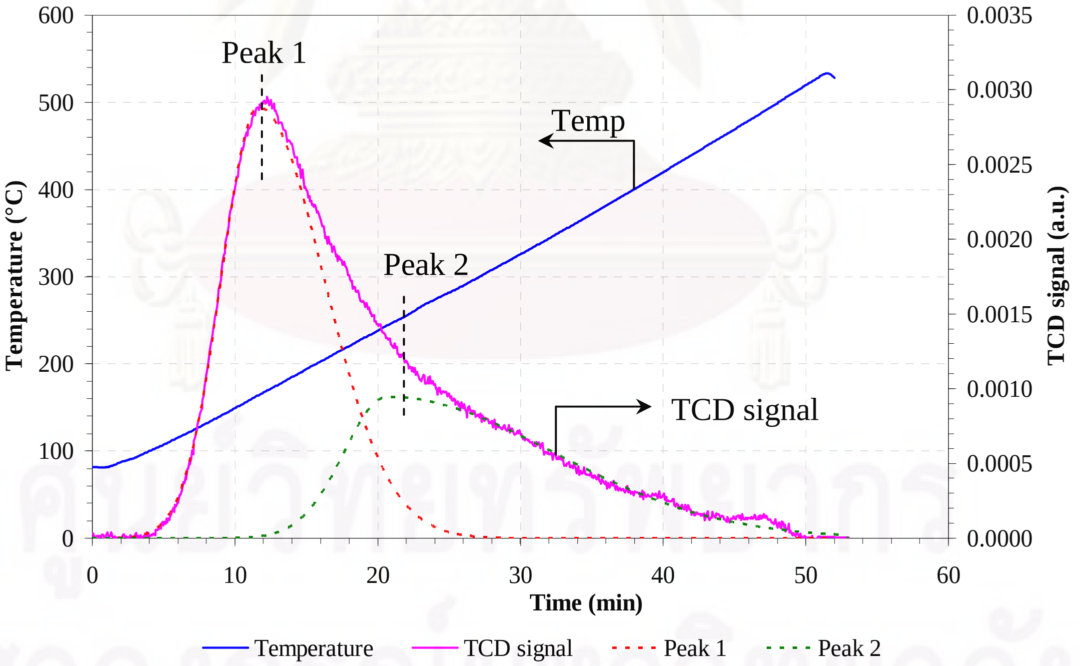


Figure 4.26 NH_3-TPD of Co-TS-1(2050)

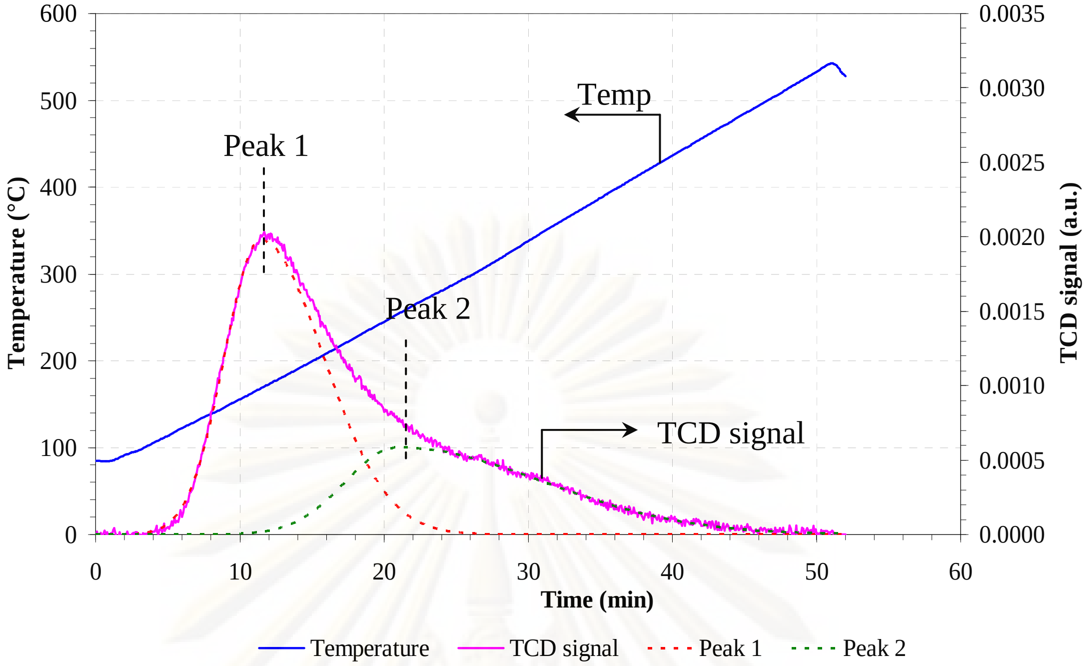


Figure 4.27 NH_3-TPD of Co-TS-1(1377)

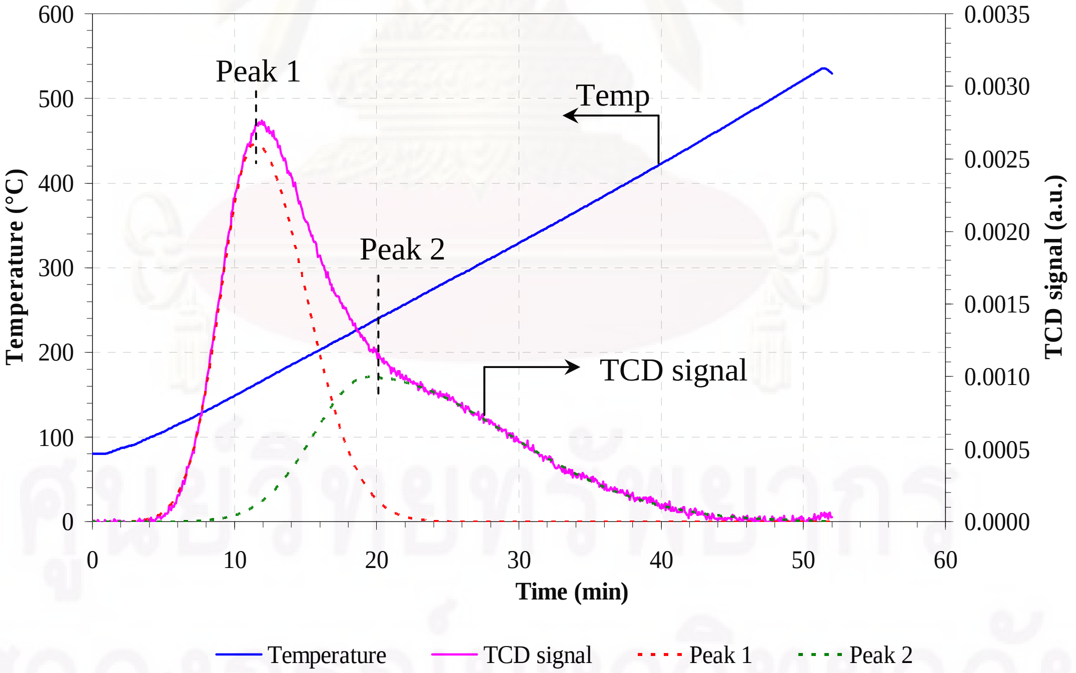


Figure 4.28 NH_3-TPD of Co-TS-1(1292)

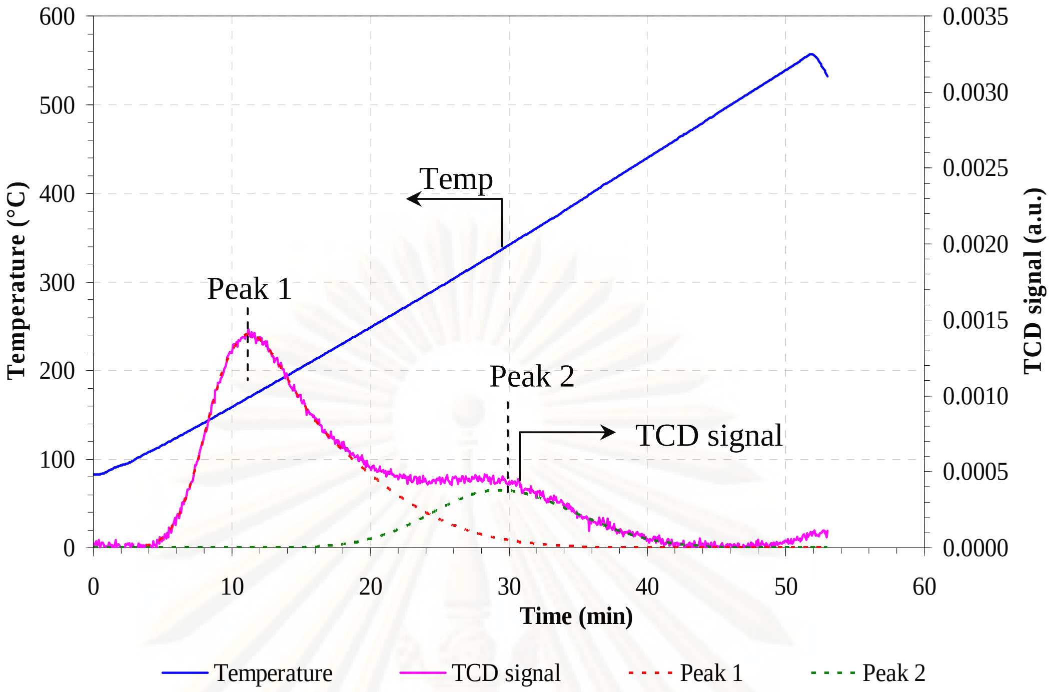


Figure 4.29 NH_3-TPD of Co-TS-1(1233)

4.4 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 Co-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 4.30**. To explain the formation of cresol and benzaldehyde, the following 2 mechanisms are proposed:

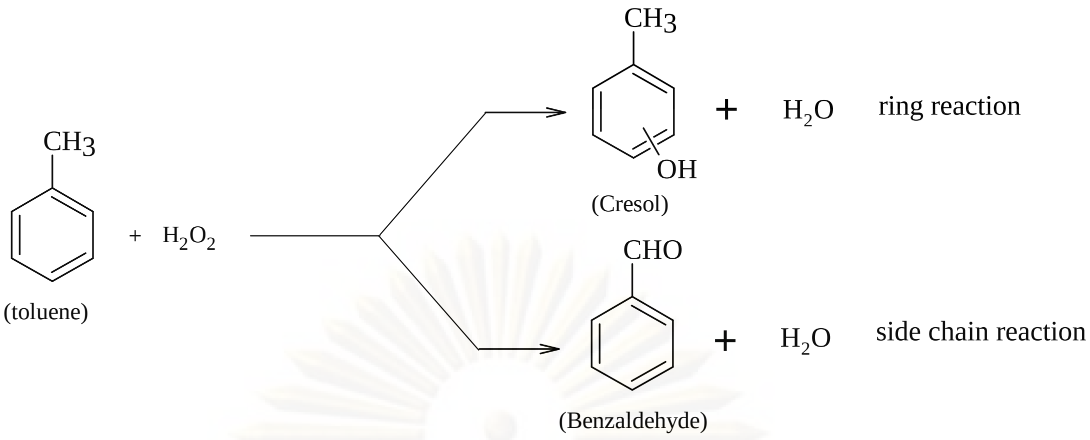


Figure 4.30 The two parallel reactions of hydroxylation of toluene

The first possible mechanism for the formation of o-cresol and p-cresol over TS-1 and Co-TS-1 are showed in **Figure 4.31**. This mechanism follows the electrophilic substitution of benzene ring. The mechanism of the formation of cresol is proposed to consist of the following four steps:

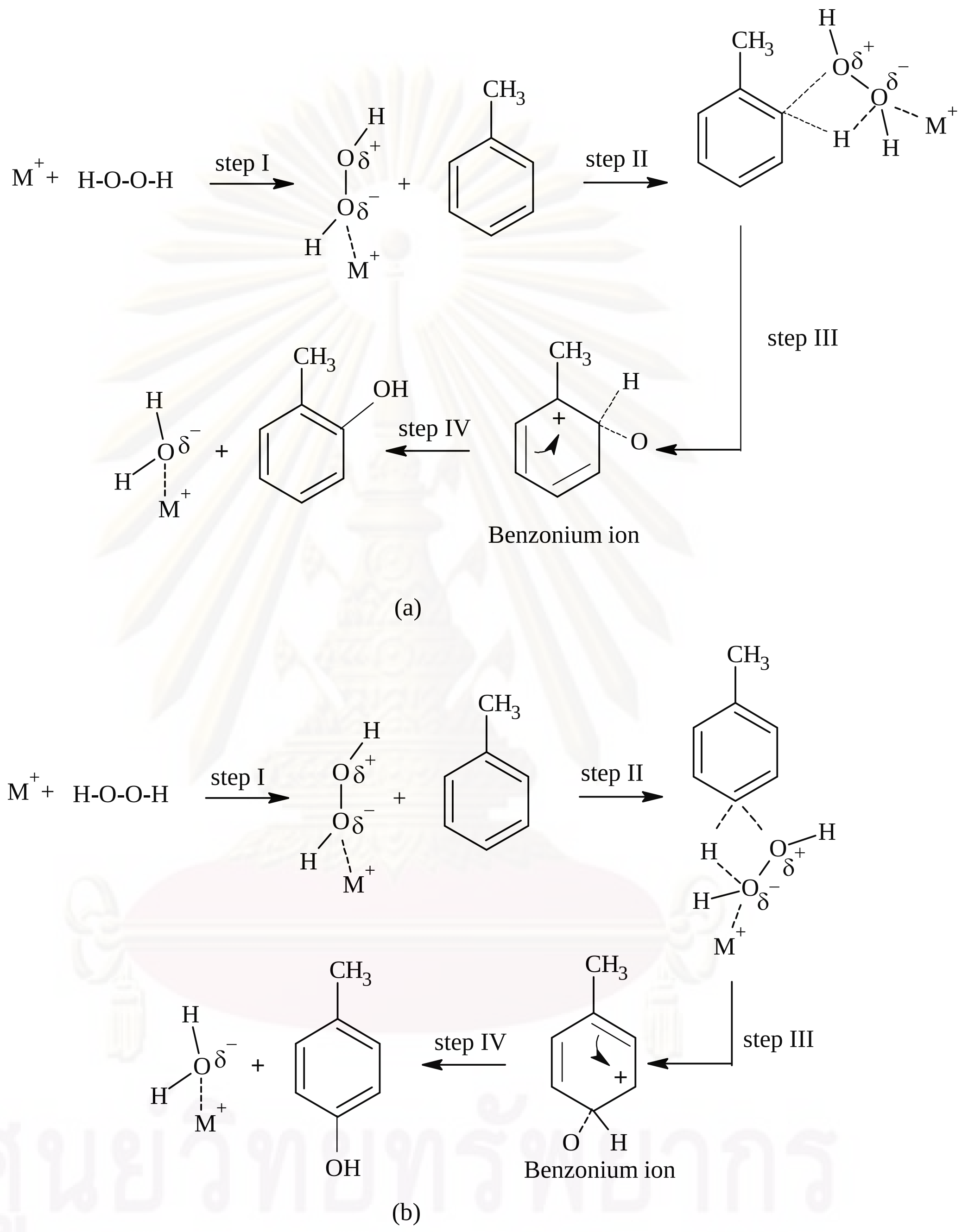
Step (i) The metal active site convert hydrogen peroxide to a strong electrophile by forming a complex and polarizing the (OH)-(OH) bond.

Step (ii) 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 from 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.

Step (iii) 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.

Step (iv) The substitution is completed by loss of a proton from sp^3 carbon atom, the same atom to which the electrophilic became attached.

The reaction proceeds via this mechanism should produce only cresol.



Where M^{+} is Ti^{4+} and Co^{3+}

Figure 4.31 The mechanism for the formation of cresol in the hydroxylation of toluene (a) o-cresol formation and (b) p-cresol formation. Co^{3+} is more preferred than Co^{2+} due to Co^{3+} has stronger positive charge than Co^{2+}.

The second mechanism is proceeds via the formation of hydroxyl radical (·OH) and hydrogen peroxide radical (·OOH). The reaction pathways of this mechanisms depends on the cation involves.

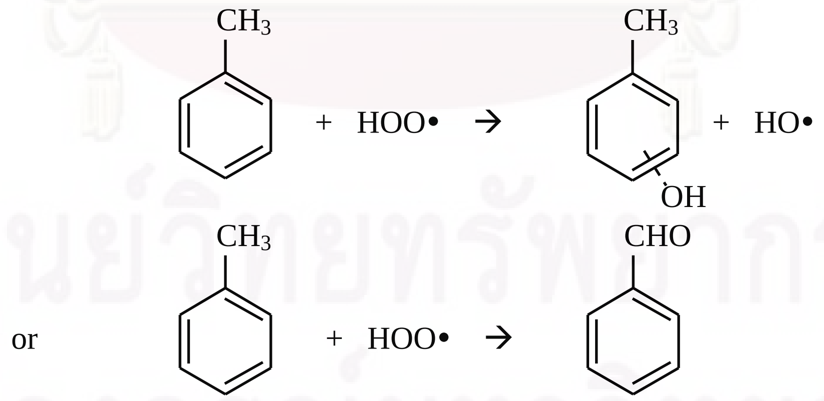
Over Ti cation.

1. Ti on the catalyst surface already exists in Ti^{4+} form due to this state is the most stable state.

2. The metal active site, Ti^{4+}, converts hydrogen peroxide to a strong electrophile by forming a hydrogen peroxide radical (·OOH). Ti^{4+} is converted to Ti^{3+} in this reaction step.

$$Ti^{4+} + HOOH \rightarrow Ti^{3+} + HOO\bullet + H^+$$

3. The electrophile (·OOH) occurs in step (2) attacks a carbon atom of the benzene ring of toluene (at either ortho- or para- position) or the carbon atom of the methyl group. The substitution at the aromatic ring is completed by the loss of a hydrogen atom from the aromatic ring to produce o-cresol or p-cresol and ·OH (hydroxyl free radical). The attack at the methyl group will form benzyl alcohol and ·OH free radial. Since no benzyl alcohol is found in the reaction product, it is believe that benzyl alcohol is rapidly oxidized to benzaldehyde.



4. The Ti^{3+} from step (2) is oxidized by the hydroxyl radical (•OH) from step (3) and return to Ti^{4+} again. Due to Ti^{3+} has less stability than Ti^{4+}, this reaction should be fast.

$$Ti^{3+} + HO\bullet \rightarrow Ti^{4+} + OH^-$$

Over Co cation.

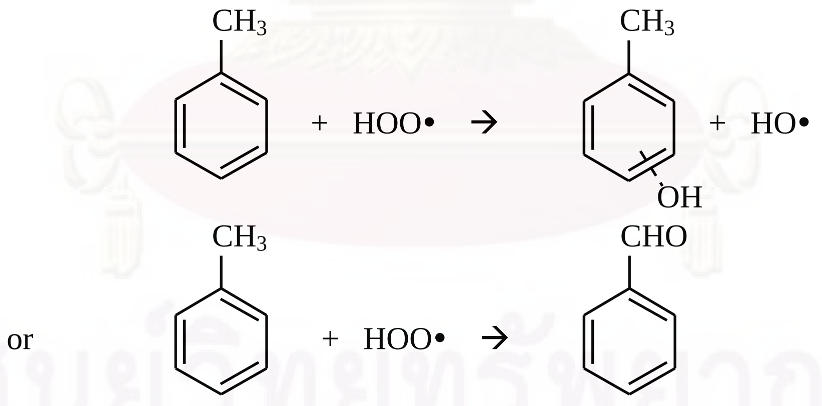
1. Since Co^{2+} is more stable than Co^{3+}, only some Co^{2+} in Co-TS-1 catalyst can be oxidized by oxygen during the calcination of the catalyst to become Co^{3+}.

$$Co^{2+} + O_2 \rightarrow Co^{3+} + O^{2-}$$

2. The metal active site, Co^{3+}, converts hydrogen peroxide to a strong electrophile by forming a hydrogen peroxide radical (·OOH). Co^{3+} is converted to Co^{2+} in this reaction step.

$$Co^{3+} + HOOH \rightarrow Co^{2+} + HOO\bullet + H^+$$

3. The electrophile (·OOH) occurs in step (2) attacks a carbon atom of the benzene ring of toluene (at either ortho- or para- position) or the carbon atom of the methyl group. The substitution at the aromatic ring is completed by the loss of a hydrogen atom from the aromatic ring to produce o-cresol or p-cresol and ·OH (hydroxyl free radical). The attack at the methyl group will form benzyl alcohol and ·OH free radial. Since no benzyl alcohol is found in the reaction product, it is believe that benzyl alcohol is rapidly oxidized to benzaldehyde.



4. The Co^{2+} from step (2) is oxidized by the hydroxyl radical (•OH) from step (3) and return to Co^{3+} again. Since Co^{2+} has higher stability than Co^{3+}, this step should be slow.

$$Co^{2+} + HO\bullet \rightarrow Co^{3+} + OH^-$$

Therefore, the second mechanism can produce both cresols and benzaldehyde.

It is known that in the absence of any transition metal cation, the self decomposition reaction of H_2O_2 can be attenuated by adding some acid into the H_2O_2 solution. In the presence of several transition metal cation in the aqueous H_2O_2 solution, H_2O_2 can decompose catalytically very fast. When the transition metal cation is in the form of ion fixed on a solid surface, the acidity of the solution may change the structure of that cation which results in the promotion of H_2O_2 decomposition also. The addition of acid to the reaction mixture may encourage the second pathway which subsequently produces more ·OOH and ·OH free radicals. Due to the fact that both ·OOH and ·OH radicals can freely attack any part of toluene molecule and the hydrogen atom of the methyl group can be removed much more easily than the hydrogen atom of the aromatic ring, more benzaldehyde is produced when acid is added to the reaction mixture. In reality, the mechanism decomposition of H_2O_2 over some solid oxide catalyst such as manganese oxides and iron oxides is still a subject of study (Laat and Gallard (1999), Sunglin and Gurol (1998), Broughton and Wentworth (1947), Broughton et al. (1947)). To the best of our knowledge, up to present there is still no mechanism generally accepted.

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

In this study, the TS-1 and TS-1 modified with cobalt metal are prepared and investigated. The catalytic activity is evaluated using with the reaction between toluene and hydrogen peroxide. The effect of catalytic activity due to acidity of solution, reaction temperature and amount of hydrochloric acid added are examined. The first part of this chapter presents the experimental result and discussion. At the end of this research the following conclusions and suggestion for future work are drawn and summarized in the second section.

5.1 Conclusions

1. Cobalt cation can be incorporated into the MFI structure of TS-1 without destroying the MFI structure.

2. The reaction pathway in the hydroxylation has two paths. The first path 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. The proton (H^+) really affects the reaction between toluene and hydrogen peroxide, not the anion (Cl^-), by enhancing catalytic activity of the catalysts.

4. The appearance of acid in the aqueous solution enhances the H_2O_2 conversion significantly and promotes benzaldehyde production for all catalysts.

5. For the reaction with and without acid in the solution, the H_2O_2 conversion increases with the increase of reaction temperature but will also increase benzaldehyde selectivity.

6. The H_2O_2 conversion will depend on the amount of hydrochloric acid.

5.2 Recommendation

From the previous summarization, 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.

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APPENDICES

APPENDIX A

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 (Topic 3.1.2).

Molecular Weight of Si = 28.0855

Molecular Weight of SiO_2 = 60.0843

Weight percent of SiO_2 in sodium Silicate = 28.5

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

$$\text{mole of Si used} = \text{wt.} \times \frac{(\%)}{100} \times \frac{(\text{M.W. of Si})}{(\text{M.W. of } SiO_2)} \times \frac{(1\,\text{mole})}{(\text{M.W. of Si})}$$

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

$$= 0.3273$$

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/Co atomic ratio of 150 by using $Co(NO_3)_2.6H_2O$ for cobalt source.

Molecular weight of Co = 58.93

Molecular weight of $Co(NO_3)_2.6H_2O$ = 291.03

Si/Co atomic ratio = 150

Mole of $Co(NO_3)_2.6H_2O$ required =0.3273/150

= 2.18×10^{-3} mole

Amount of $Co(NO_3)_2.6H_2O$ = $(2.18 \times 10^{-3}) \times (291.03)$

= 0.635 g

which used in A1 and A2 solutions.

APPENDIX B

CALCULATION OF METAL QUANTITY

Example of the calculation of the metal quantity in catalyst

The X-Ray Fluorescence Spectrometer (XRF) results were reported in the amount of metal oxide as shown in **Table B1**.

Table B1 Data of TS-1 from XRF technique and the molecular weights of the metal oxides

Metal oxide	Concentration (% wt)	Molecular weight(MW)
Na_2O	0.964	61.98
Al_2O_3	0.089	101.96
SiO_2	96.177	60.08
SO_3	0.132	80.06
CaO	0.013	56.08
TiO_2	2.593	79.86
Fe_2O_3	0.032	159.69

1. Mole of metal oxides

$$\text{Mole of } Na_2O = \frac{\text{weight of } Na_2O}{\text{molecular weight of } Na_2O}$$

$$\text{Mole of } Na_2O = \frac{0.964}{61.9790} = 0.0155 \text{ mole}$$

2. Mole of cation (e.g. Sodium: Na)

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

$$\text{Mole of Na} = (1) \times (0.0155)$$

$$= 0.0155 \text{ mole}$$

3. Mole percent of cation (e.g. Sodium: Na)

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

$$\text{Mole \% of Na} = \frac{0.0155}{6.5519} = 0.002374 \text{ mole\%}$$

Calculated moles of metal oxide, mole of cation and mole% of cation are illustrated in **Table B2**.

Table B2 Calculated moles of metal oxide, mole of cation and mole% of cation of TS-1

TS-1			**Mole of metal oxide**	**Mole of cation**	**Mole % of cation**	**Mol %**
Compound	**% wt**	**MW**				
Na_2O	0.964	61.98	0.01555	0.01555	0.00237	0.2374
Al_2O_3	0.089	101.96	0.00087	0.00262	0.00040	0.0399
SiO_2	96.177	60.08	1.60070	6.40280	0.97724	97.7243
SO_3	0.132	80.06	0.00164	-	-	-
CaO	0.013	56.08	0.00023	0.00046	0.00007	0.0071
TiO_2	2.593	79.86	0.03246	0.12986	0.01982	1.9821
Fe_2O_3	0.032	159.69	0.00020	0.00060	0.00009	0.0092

Table B3 Calculated moles of metal oxide, mole of cation and mole% of cation of Co-TS-1(2050)

Co-TS-1(200)			Mole of metal oxide	Mole of cation	Mole % of cation	Mol %
Compound	% wt	MW				
Al_2O_3	0.078	101.96	0.00077	0.00229	0.00035	0.0351
SiO_2	96.143	60.08	1.60013	6.40054	0.97911	97.9108
SO_3	0.984	80.06	0.01230	-	-	-
TiO_2	2.583	79.87	0.03234	0.12936	0.01979	1.9789
Fe_2O_3	0.095	159.69	0.00060	0.00178	0.00027	0.0273
CoO	0.117	74.93	0.00156	0.00312	0.00048	0.0478

Table B4 Calculated moles of metal oxide, mole of cation and mole% of cation of Co-TS-1(1377)

Co-TS-1(150)			Mole of metal oxide	Mole of cation	Mole % of cation	Mol %
Compound	% wt	MW				
Na_2O	0.670	61.98	0.01081	0.01081	0.00165	0.1650
Al_2O_3	0.110	101.96	0.00108	0.00323	0.00049	0.0494
SiO_2	96.039	60.08	1.59840	6.39361	0.97638	97.6380
SO_3	0.271	80.06	0.00338	-	-	-
TiO_2	2.703	79.86	0.03384	0.13538	0.02067	2.0674
Fe_2O_3	0.032	159.69	0.00020	0.00060	0.00009	0.0092
CoO	0.174	74.93	0.00232	0.00464	0.00071	0.0709

Table B5 Calculated moles of metal oxide, mole of cation and mole% of cation of Co-TS-1(1292)

Co-TS-1(100)			**Mole of metal oxide**	**Mole of cation**	**Mole % of cation**	**Mol %**
Compound	**% wt**	**MW**				
Al_2O_3	0.098	101.96	0.00096	0.00288	0.00044	0.0440
SiO_2	96.325	60.08	1.60316	6.41266	0.97762	97.7629
SO_3	0.597	80.06	0.00745	-	-	-
CoO	0.186	74.93	0.00248	0.00496	0.00076	0.0757
TiO_2	2.760	79.86	0.03456	0.13823	0.02107	2.1074
Fe_2O_3	0.035	159.69	0.00022	0.00066	0.00010	0.0100

Table B6 Calculated moles of metal oxide, mole of cation and mole% of cation of Co-TS-1(1233)

Co-TS-1(50)			**Mole of metal oxide**	**Mole of cation**	**Mole % of cation**	**Mol %**
Compound	**% wt**	**MW**				
Al_2O_3	0.128	101.96	0.00126	0.00377	0.00057	0.0570
SiO_2	97.916	60.08	1.62964	6.51857	0.98593	98.5927
SO_3	0.056	80.06	0.00070	-	-	-
CaO	0.013	56.08	0.00023	0.00046	0.00007	0.0070
TiO_2	1.655	79.86	0.02072	0.08289	0.01254	1.2537
Fe_2O_3	0.034	159.69	0.00021	0.00064	0.00010	0.0097
CoO	0.198	74.93	0.00264	0.00528	0.00079	0.0799

APPENDIX C

DATA OF CALCULATION OF ACID SITE

The NH_3-TPD profile is deconvolved using a “fityk” deconvolution programme after base line substraction. The results obtained from the programme suggest that the acidic site can categorized into 2 groups, according to their desorption peaks. The first one locates around 160-200 °C which will be named here “the weak acid site” and the second one locates higher than 200 °C which will be named here “the strong acid site”. The amount of acid site can calculate from areas of each peak. The areas that observe from NH_3-TPD are showed in **Table C1**.

Table C1 Reported peak area from Micromeritrics Chemisorb 2750 (NH_3-TPD)

Catalyst	Temp.	Area of weak acid	Temp.	Area of strong acid
TS-1	190	0.01128	343	0.00140
Co-TS1(2050)	164	0.02589	246	0.01740
Co-TS1(1377)	168	0.01702	253	0.01004
Co-TS1(1292)	161	0.01946	233	0.01004
Co-TS1(1233)	171	0.01522	338	0.00493

The calibration curve for calculate acid site from NH_3-TPD is exhibited in **Figure C1.** The amount of NH_3 (ml) in y-axis and area reported by NH_3-TPD in x-axis are exhibited in the curves.

Calibration curve

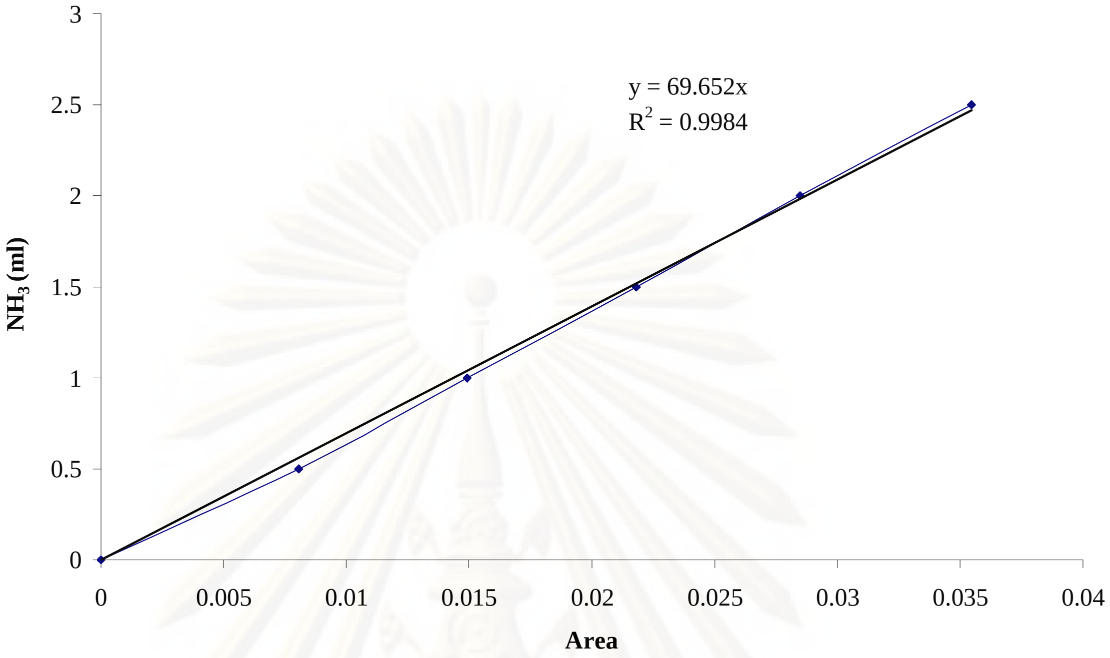


Figure C1 The calibration curve of NH_3

Calculation of total acid sites

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

1. Conversion of total peak area to peak volume

Conversion from calibration curve of Micromeritrics Chemisorb 2750, peak area of TS-1 0.01128 equal NH_3 0.7857 ml

2. Calculation for adsorbed volume of 15% NH_3

Adsorbed volume of 15% NH_3 = 0.15 × total peak volume
= 0.15 × 0.7857 ml
= 0.11785 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 , 0.1015 g of this sample was measured, therefore

$$\text{Total acid sites} = \frac{0.11785\ \text{ml} \times 101.325\ \text{Pa}}{\left(8.314 \times 10^{-3}\ \frac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}}\right) \times 298\ \text{K} \times (0.1015\ \text{g})}$$

$$= 47.48\ \mu\text{mol H}^{+}/\text{g}$$

APPENDIX D

CALCULATION OF CONVERSION AND PRODUCT SELECTIVITY

The catalyst performance for the reaction between toluene and hydrogen peroxide was evaluated in conversion for terms of activity.

1. The percentage of H_2O_2 conversion

$$\%\,H_2O_2 \text{ convert to product } = \frac{(2\times \text{Mole of benzaldehyde}) + \text{Mole of cresol}}{\text{Overall mole of } H_2O_2} \times 100 \quad \text{(D1)}$$

Where overall mole of product can be measured as follows:

Overall mole of benzaldehyde

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

Overall mole of o-cresol

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

Overall mole of p-cresol

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

Where mole of benzaldehyde, o-cresol, and p-cresol can be measured employing the calibration curve in **Figure E1**, **E2** and **E3** respectively, **Appendix E**.

Mole of benzaldehyde

$= ((\text{Area of benzaldehyde peak from integrator plot on GC-9A}) \times 1.0\times10^{-13})$ (D5)

Mole of o-cresol

$= ((\text{Area of o-cresol peak from integrator plot on GC-9A}) \times 1.0\times10^{-13})$ (D6)

Mole of p-cresol

= ((Area of p-cresol peak from integrator plot on GC-9A) 9.0×10^{-14}) (D7)

Therefore,

Mole of all products

= (mole of benzaldehyde + mole of o-cresol+ mole of p-cresol) (D8)

Where overall mole of H_2O_2 can be measured as follows:

$$\text{Overall mole of } H_2O_2 = \frac{\text{Volume of } H_2O_2 \text{ feeding} \times \text{Density of } H_2O_2}{\text{Molecular weight of } H_2O_2} \quad \text{(D9)}$$

$$\text{Overall mole of } H_2O_2 = \frac{\text{Volume of } H_2O_2 \text{ feeding} \times 1.44}{34.02}$$

2. The percentage of product selectivity

Where selectivity of o-cresol can be measured as follows:

$$\%\text{Selectivity of o-cresol} = \frac{\text{mole of o-cresol}}{\text{overall mole of product}} \times 100 \quad \text{(D10)}$$

3. The percentage of productivity

$$\text{Productivity of benzaldehyde} = \frac{\text{mole of benzaldehyde}}{\text{weight catalyst (g)} \times 120\ \text{min} \times 10^{-6}} \quad \text{(D11)}$$

APPENDIX E

CALIBRATION CURVES

This appendix shows the calibration curves for calculation of products in reaction between toluene and hydrogen peroxide. The main product is benzaldehyde, o-cresol and p-cresol.

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

Mole of standard (pure benzaldehyde, pure o-cresol and pure p-cresol) in y-axis and area reported by gas chromatography in x-axis are exhibited in the curves. The calibration curves of benzaldehyde, o-cresol and p-cresol are illustrated in the **Figures E1-E3**, respectively.

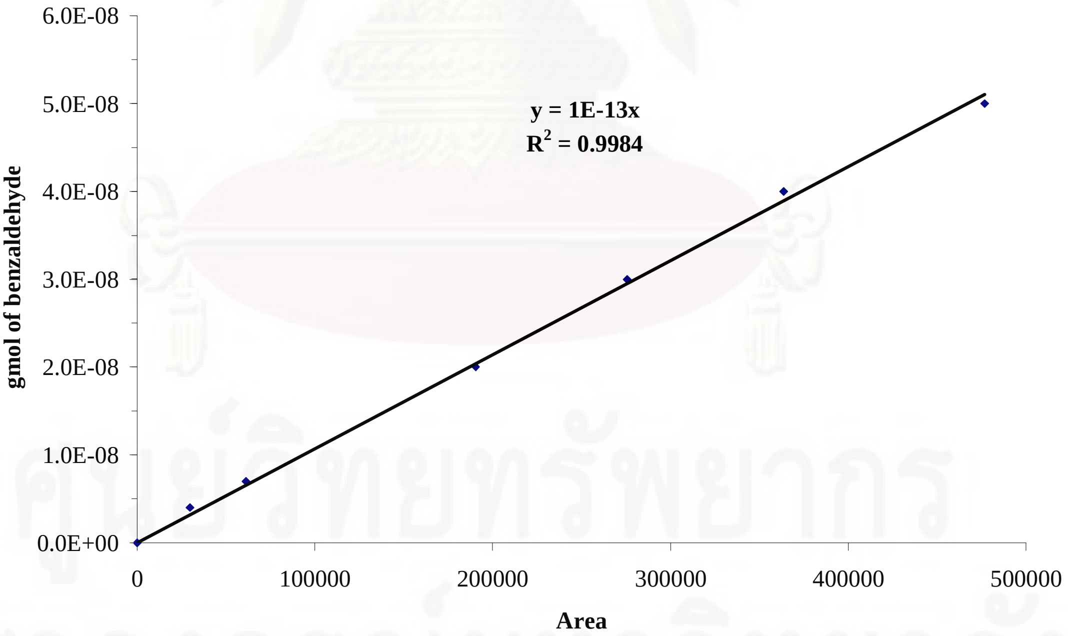


Figure E1 The calibration curve of benzaldehyde

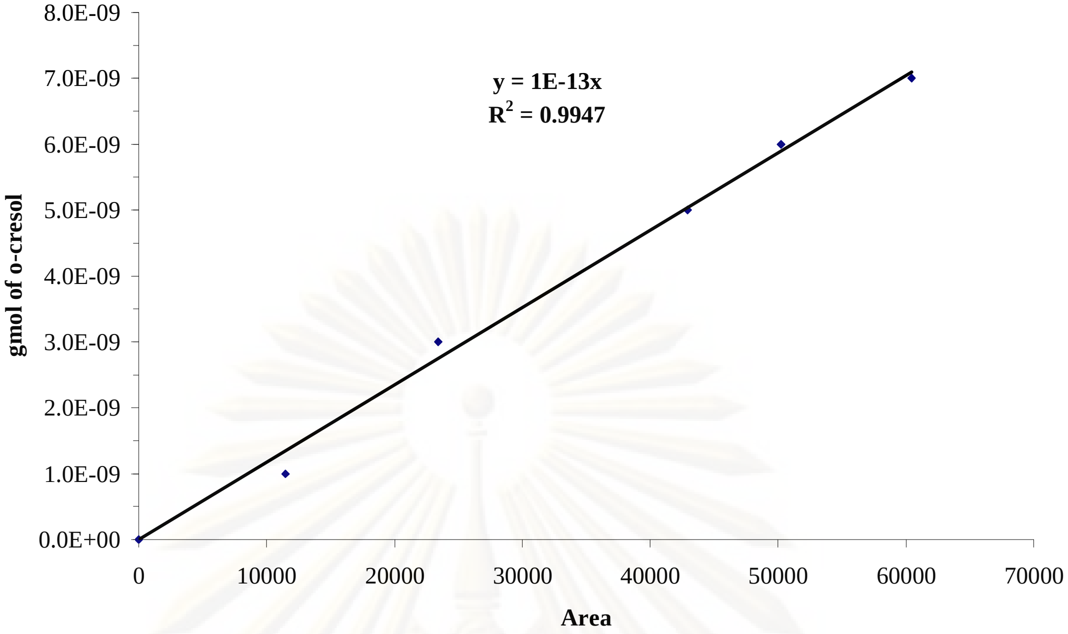


Figure E2 The calibration curve of o-cresol

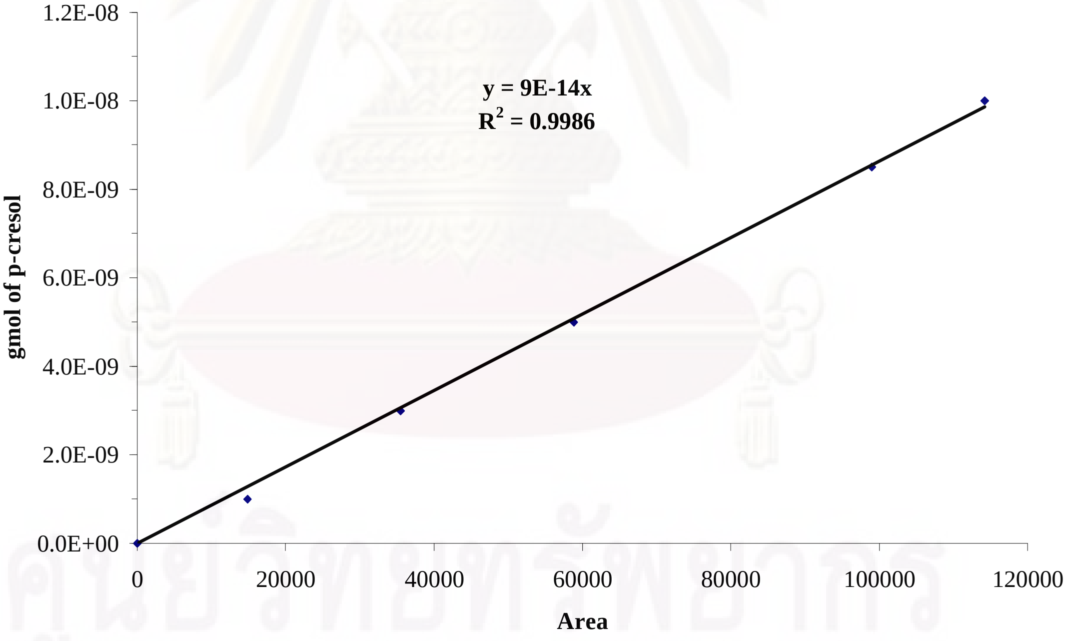


Figure E3 The calibration curve of p-cresol

APPENDIX F

DATA OF EXPERIMENTS

Table F1 Data of Figure 4.4

Solution	% Total hydrogen peroxide convert to product at 90°C
	Catalyst: TS-1
Pure water	0.3770
HCl 10 ml	2.2440
NaCl 10 ml	0.3325

Table F2 Data of Figure 4.5

Solution	Productivity at 90°C (µmoles/min)		
	Catalyst: TS-1		
	Benzaldehyde	o-cresol	p-cresol
Pure water	0.0657	0.8470	0.0720
HCl 10 ml	0.0939	0.0620	0.0603
NaCl 10 ml	0.0819	0.0729	0.0669

Table F3 Data of Figure 4.6

Solution	Productivity at 90°C (µmoles/min)		
	Catalyst: TS-1		
	Benzaldehyde	o-cresol	p-cresol
Pure water	27.21	86.26	36.13
HCl 10 ml	38.88	6.31	30.28
NaCl 10 ml	33.91	7.43	33.59

Table F4 Data of Figure 4.7

Catalyst	% Total hydrogen peroxide convert to products at 70°C	
	Pure water	HCl 10 ml
TS-1	0.4208	1.2799
Co-TS-1(2050)	0.8298	0.9956
Co-TS-1(1377)	0.8156	0.8789
Co-TS-1(1292)	0.7861	1.3291
Co-TS-1(1233)	0.8658	0.9707

Table F5 Data of Figure 4.8

Catalyst	Productivity at 70°C (μmoles/min)					
	Pure water			HCl 10 ml		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
TS-1	0.0342	0.1170	0.1578	0.2966	0.1358	0.3142
Co-TS-1 (2050)	0.1551	0.1579	0.2076	0.2588	0.1139	0.1806
Co-TS-1 (1377)	0.0677	0.2699	0.2589	0.1912	0.1427	0.1913
Co-TS-1 (1292)	0.0888	0.2214	0.2419	0.3843	0.1227	0.1924
Co-TS-1 (1233)	0.0826	0.2625	0.2763	0.2136	0.1665	0.1966

Table F6 Data of Figure 4.9

Catalyst	%Selectivity at 70°C					
	Pure water			HCl 10 ml		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
TS-1	11.05	37.87	51.08	39.72	18.19	42.08
Co-TS-1 (2050)	29.80	30.33	39.88	46.78	20.59	32.63
Co-TS-1 (1377)	11.34	45.25	43.41	36.41	27.17	36.43
Co-TS-1 (1292)	16.08	40.11	43.81	54.94	17.54	27.51
Co-TS-1 (1233)	13.29	42.24	44.46	37.04	28.88	34.08

Table F7 Data of Figure 4.10

Catalyst	% Total hydrogen peroxide convert to products at 90°C	
	Pure water	HCl 10 ml
TS-1	0.3770	2.2441
Co-TS-1(2050)	1.3010	1.8821
Co-TS-1(1377)	0.9105	1.5268
Co-TS-1(1292)	0.8086	1.6802
Co-TS-1(1233)	0.8891	1.5095

Table F8 Data of Figure 4.11

Catalyst	Productivity at 90°C (µmoles/min)					
	Pure water			HCl 10 ml		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
TS-1	0.0657	0.0939	0.0819	0.8470	0.0620	0.0729
Co-TS-1 (2050)	0.4089	0.1432	0.0993	0.7072	0.0537	0.0663
Co-TS-1 (1377)	0.1825	0.2588	0.1180	0.5692	0.0579	0.0457
Co-TS-1 (1292)	0.2409	0.1256	0.0477	0.6310	0.0684	0.0382
Co-TS-1 (1233)	0.1621	0.2471	0.1510	0.5603	0.0540	0.0552

Table F9 Data of Figure 4.12

Catalyst	%Selectivity at 90°C					
	Pure water			HCl 10 ml		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
TS-1	27.21	38.88	33.91	86.26	6.31	7.43
Co-TS-1 (2050)	62.78	21.98	15.24	85.49	6.49	8.01
Co-TS-1 (1377)	32.63	46.28	21.10	84.61	8.60	6.79
Co-TS-1 (1292)	58.15	30.33	11.52	85.55	9.28	5.18
Co-TS-1 (1233)	28.93	44.11	26.96	83.68	8.07	8.25

Table F10 Data of Figure 4.13

Catalyst	% Total hydrogen peroxide convert to products without acid	
	70°C	90°C
TS-1	0.4208	0.3770
Co-TS-1(2050)	0.8298	1.3010
Co-TS-1(1377)	0.8156	0.9105
Co-TS-1(1292)	0.7861	0.8086
Co-TS-1(1233)	0.8658	0.8891

Table F11 Data of Figure 4.14

Catalyst	Productivity without acid (μmoles/min)					
	70°C			90°C		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
TS-1	0.0342	0.1170	0.1578	0.0657	0.0939	0.0819
Co-TS-1 (2050)	0.1551	0.1579	0.2076	0.4089	0.1432	0.0993
Co-TS-1 (1377)	0.0677	0.2699	0.2589	0.1825	0.2588	0.1180
Co-TS-1 (1292)	0.0888	0.2214	0.2419	0.2409	0.1256	0.0477
Co-TS-1 (1233)	0.0826	0.2625	0.2763	0.1621	0.2471	0.1510

Table F12 Data of Figure 4.15

Catalyst	%Selectivity without acid					
	70°C			90°C		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
TS-1	11.05	37.87	51.08	27.21	38.88	33.91
Co-TS-1 (2050)	29.80	30.33	39.88	62.78	21.98	15.24
Co-TS-1 (1377)	11.34	45.25	43.41	32.63	46.28	21.10
Co-TS-1 (1292)	16.08	40.11	43.81	58.15	30.33	11.52
Co-TS-1 (1233)	13.29	42.24	44.46	28.93	44.11	26.96

Table F13 Data of Figure 4.16

Catalyst	% Total hydrogen peroxide convert to products with acid	
	70°C	90°C
TS-1	1.2799	2.2441
Co-TS-1(2050)	0.9956	1.8821
Co-TS-1(1377)	0.8789	1.5268
Co-TS-1(1292)	1.3291	1.6802
Co-TS-1(1233)	0.9707	1.5095

Table F14 Data of Figure 4.17

Catalyst	Productivity with acid (µmoles/min)					
	70°C			90°C		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
TS-1	0.2966	0.1358	0.3142	0.8470	0.0620	0.0729
Co-TS-1 (2050)	0.2588	0.1139	0.1806	0.7072	0.0537	0.0663
Co-TS-1 (1377)	0.1912	0.1427	0.1913	0.5692	0.0579	0.0457
Co-TS-1 (1292)	0.3843	0.1227	0.1924	0.6310	0.0684	0.0382
Co-TS-1 (1233)	0.2136	0.1665	0.1966	0.5603	0.0540	0.0552

Table F15 Data of Figure 4.18

Catalyst	%Selectivity with acid					
	70°C			90°C		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
TS-1	39.72	18.19	42.08	86.26	6.31	7.43
Co-TS-1 (2050)	46.78	20.59	32.63	85.49	6.49	8.01
Co-TS-1 (1377)	36.41	27.17	36.43	84.61	8.60	6.79
Co-TS-1 (1292)	54.94	17.54	27.51	85.55	9.28	5.18
Co-TS-1 (1233)	37.04	28.88	34.08	83.68	8.07	8.25

Table F16 Data of Figure 4.19

Amount of acid	% Total hydrogen peroxide convert to products
	Catalyst: TS-1
Pure water	0.3770
HCl 5 ml	2.0363
HCl 10 ml	2.2441
HCl 20 ml	2.3095
HCl 40 ml	1.8457

Table F17 Data of Figure 4.20

Amount of acid	Productivity (µmoles/min)		
	Catalyst: TS-1		
	Benzaldehyde	o-cresol	p-cresol
Pure water	0.0658	0.0940	0.0820
HCl 5 ml	0.7586	0.0649	0.0773
HCl 10 ml	0.8470	0.0620	0.0729
HCl 20 ml	0.8984	0.0427	0.0407
HCl 40 ml	0.7380	0.0165	0.0111

Table F18 Data of Figure 4.21

Amount of acid	%Selectivity		
	Catalyst: TS-1		
	Benzaldehyde	o-cresol	p-cresol
Pure water	27.21	38.88	33.91
HCl 5 ml	84.21	7.21	8.58
HCl 10 ml	86.26	6.31	7.43
HCl 20 ml	91.51	4.35	4.14
HCl 40 ml	96.40	2.15	1.45

Table F19 Data of Figure 4.22

Amount of acid	% Total hydrogen peroxide convert to products
	Catalyst: Co-TS-1(1377)
Pure water	0.9105
HCl 5 ml	1.4974
HCl 10 ml	1.5268
HCl 20 ml	1.6727
HCl 40 ml	1.5222

Table F20 Data of Figure 4.23

Amount of acid	Productivity (µmoles/min)		
	Catalyst: Co-TS-1(1377)		
	Benzaldehyde	o-cresol	p-cresol
Pure water	0.1825	0.2588	0.1180
HCl 5 ml	0.5068	0.1130	0.0934
HCl 10 ml	0.5692	0.0579	0.0457
HCl 20 ml	0.6342	0.0496	0.0463
HCl 40 ml	0.6008	0.0141	0.0251

Table F21 Data of Figure 4.24

Amount of acid	%Selectivity		
	Catalyst: Co-TS-1(1377)		
	Benzaldehyde	o-cresol	p-cresol
Pure water	32.63	46.28	21.10
HCl 5 ml	71.07	15.84	13.09
HCl 10 ml	84.61	8.60	6.79
HCl 20 ml	86.87	6.79	6.34
HCl 40 ml	93.86	2.21	3.93

APPENDIX G

MATERIAL SAFETY DATA SHEET

Toluene

Safety data for toluene

General

Synonyms: methylbenzene, phenylmethane, toluol, antisal 1A, CP 25, methacide, methylbenzol, NCI-C07272, RCRA waste number U220, tolu-sol

Molecular formula: $C_6H_5(CH_3)$

Physical data

Appearance: Colourless liquid with a benzene-like odour (odour threshold 0.17 ppm)

Melting point: -93 ºC

Boiling point: 110.6 ºC

Specific gravity: 0.865

Vapour pressure: 22 mm Hg at 20 ºC (vapour density 3.2)

Flash point: 4 ºC

Explosion limits: 1% - 7%

Autoignition temperature: 536 ºC

Stability

Stable. Substances to be avoided: oxidizing agents, oxygen and moisture. Highly flammable. Hygroscopic.

Toxicology

Harmful if inhaled, especially if breathed in over long periods. May cause drowsiness. Possible risk of harm to the unborn child. May cause lung damage if swallowed. Serious irritant.

Personal protection

Safety glasses. Good ventilation.

Hydrogen Peroxide, 30% solution

Safety data for hydrogen peroxide, 30% solution

General

Synonyms: albone 30, albone 35, albone 50, albone 70, albone 35cg, albone 50cg, albone 70cg, interox, kastone, perone 30, perone 35, perone 50. Data also applies to solutions of similar strength. 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: ca. -28 °C
Boiling point: ca. 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.

Personal protection

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

Benzaldehyde

Safety data for bezaldehyde

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

o-cresol

Safety data for 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: $C_6H_4(CH_3)(OH)$

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

Safety data for 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: C_6H_4 CH_3OH

Physical data

Appearance: crystals
Melting point: 34 ºC
Boiling point: 202 ºC
Vapour density: 3.7 (air = 1)
Vapour pressure: 0.1 mm Hg at 20 ºC
Density (g cm-3): 1.03
Flash point: 86 (closed cup)
Explosion limits:
Autoignition temperature:
Water solubility: moderate

Stability

Stable. Combustible. Incompatible with strong oxidizing agents. Light-sensitive.

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. Experimental neoplastigen. May cause serious eye damage. Severe skin and eye irritant.

Personal protection

Safety glasses, gloves, adequate ventilation.

Titanium (IV) n-butoxide

Safety data for p-cresol

General

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

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

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

Physical data

Boiling point : 310-314 °C
Flash point : 78 °C
Density (g cm^{-3}) : 1.486

Toxicology

Irritating to eyes, respiratory system and skin.

Personal protection

Avoid contact with skin and eyes.

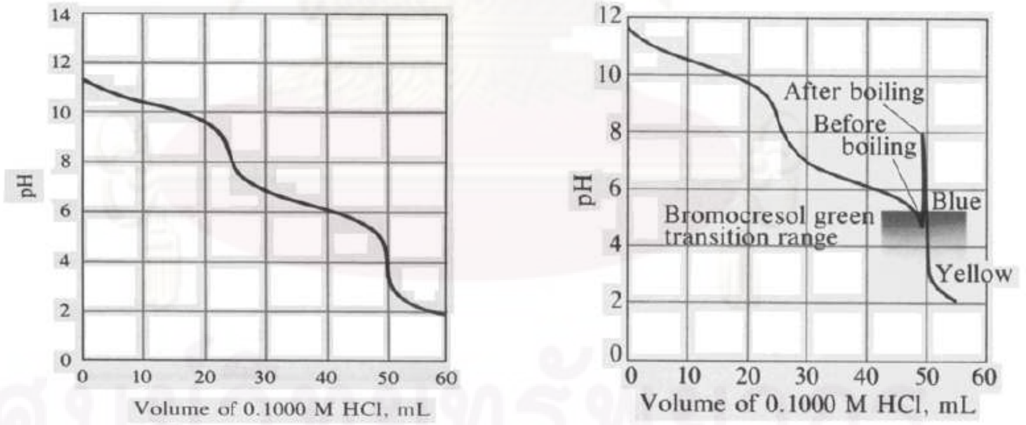
APPENDIX H

HYDROCHLORIC ACID STANDARDIZATION PROCEDURE

The hydrochloric acid 0.1M is prepare from hydrochloric acid 37% AR grade and dilute by distilled water. The certain concentration of dilute hydrochloric acid (HCl) can find by titration method, this process is known as standardising the hydrochloric acid. The titration use the anhydrous sodium carbonate solution for the standard solution and methyl red (colour change in pH 4.4 (red) – pH 6.2 (yellow)) is the indicator. The stoichiometry equation of hydrochloric acid and sodium carbonate is

$$2HCl + Na_2CO_3 \rightarrow 2NaCl + H_2O + CO_2$$

The pH change in titration hydrochloric acid 0.1 M by sodium carbonate solution 0.1 M with and without boiling to drive CO_2 are showed in **Figure H1**.



(a) (b)

Figure H1 The pH change in titration hydrochloric acid 0.1 M by sodium carbonate solution 0.1 M without boiling to drive CO_2 (a) with boiling to drive CO_2 (b) (Skoog and West, 1994)

Materials

1. Sodium carbonate (Na_2CO_3) analar grade
2. Demineralized or distilled water
3. Methyl red as indicator
4. Hydrochloric acid (HCl) 0.1 M (prepared for test reaction)

Procedures

1. Dry sodium carbonate (Na_2CO_3) in an oven at temperature 110 ºC overnight.
2. Prepare sodium carbonate solution 0.1 M 250 ml using Na_2CO_3 from (1).
3. Transfer a 10 ml of sodium carbonate solution to a 250 ml conical flask. Add a few drops of methyl red indicator solution.
4. Titrate with hydrochloric acid slowly while the solution is swirling constantly. Hydrochloric acid is added dropwise when the color began to take longer time become orange.
5. Stopped adding hydrochloric acid when the solution become strong orange but not red. Take it to boil in water bath until the colour turn to yellow again.
6. Titrate with the hydrochloric acid. The end-point of the titration is when the solution just changes from yellow to red. Read the volume of hydrochloric acid for the titration.
7. Repeat the analysis several times and calculated the concentration of hydrochloric acid according to the stoichiometry equation, 2 mol of HCl ≡ 1 mol of Na_2CO_3.

Result

Table H1 Calculation the concentration of hydrochloric acid from titration

	Volume of Na_2CO_3 (ml)	**Volume of HCl (ml)**	**Concentration of HCl (Molar)**
1st titration	10.00	19.95	0.1
2nd titration	10.00	20.00	0.1

VITA

Miss Narumon Kasemsukphaisan was born on October 19th, 1985 in Prachuabkirikhan, Thailand. She received the bachelor's degree of Chemical Engineering from Faculty of Engineering, Mahidol University in 2008. She continued her master's study at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University in June, 2008.

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