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PRODUCTION OF CRESOLS IN A ONE-STEP REACTION

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รจเรข แพทย์สาสดี: การผลิตครีซอลในปฏิกิริยาขั้นตอนเดียว (PRODUCTION OF CRESOLS IN A ONE-STEP REACTION) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.ธราธร มงคลศรี, 83 หน้า.

งานวิจัยนี้เป็นการศึกษาการสังเคราะห์ครีซอลในปฏิกิริยาขั้นตอนเดียวระหว่างโทลูอีนกับไฮโดรเจนเปอร์ออกไซด์โดยมีตัวเร่งปฏิกิริยาไทเทเนียมซิลิกาไลต์-1 ที่ได้รับการปรับปรุงด้วยโลหะโคบอลต์ในปริมาณต่าง ๆ ที่อุณหภูมิการทำปฏิกิริยา 70 และ 90 องศาเซลเซียส และอัตราส่วนโดยโมลของสารตั้งต้นระหว่างโทลูอีนและไฮโดรเจนเปอร์ออกไซด์เป็น 1:1 และ 2:1 ผลการศึกษาพบว่าสามารถเติมโลหะโคบอล์ตได้ในปริมาณสูงถึง 0.124 โดยโมลลงในตัวเร่งปฏิกิริยาไทเทเนียมซิลิกาไลต์-1 โดยไม่มีผลต่อโครงสร้างของตัวเร่งปฏิกิริยา การศึกษาความว่องไวในการทำปฏิกิริยาพบว่าตัวเร่งปฏิกิริยาที่ได้รับการปรับปรุงทุกตัวให้ผลิตภัณฑ์หลักเป็นออโธ-ครีซอล พารา-ครีซอลเป็นผลิตภัณฑ์ และเบนซาลดีไฮด์เป็นผลิตภัณฑ์ข้างเคียง ค่าการเลือกเกิดครีซอลจะลงเมื่ออุณหภูมิการทำปฏิกิริยาเพิ่มสูงขึ้น แต่ถ้าเพิ่มสัดส่วนของโทลูอีนต่อไฮโดรเจนเปอร์ออกไซด์ให้สูงขึ้นจะทำให้ค่าการเลือกเกิดครีซอลเพิ่มขึ้น ทั้งนี้เป็นเพราะโทลูอีนจะไปปกคลุมพื้นผิวของตัวเร่งปฏิกิริยา ทำให้ปริมาณไฮโดรเจนเปอร์ออกไซด์บนพื้นผิวลดลง ปฏิกิริยาการเกิดเบนซาลดีไฮด์ซึ่งต้องใช้ไฮโดรเจนเปอร์ออกไซด์มากกว่าปฏิกิริยาการเกิดครีซอลถึง 2 เท่าจึงลดลงตามไปด้วย ผลการทดลองยังแสดงให้เห็นว่าโคบอลต์ที่เติมเข้าไปในปริมาณที่พอเหมาะในตัวเร่งปฏิกิริยาไทเทเนียมซิลิกาไลต์-1 จะไปยับยั้งการเกิดเบนซาลดีไฮด์และเพิ่มการเลือกเกิดครีซอล แต่ถ้าเติมในปริมาณที่มากเกินไปจะทำให้การเกิดเบนซาลดีไฮด์เพิ่มสูงขึ้น

ภาควิชา.............วิศวกรรมเคมี.......... ลายมือชื่อนิสิต..........รจเรข แพทย์สาสดี..........
สาขาวิชา............วิศวกรรมเคมี.......... ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก..................
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ROJAREK PASSASADEE: PRODUCTION OF CRESOLS IN A ONE-STEP REACTION. THESIS ADVISOR: ASSOC.PROF. THARATHON MONGKHONSI, Ph.D., 83 pp.

This research is a study on 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 research found that the addition of Co up to 0.124 mol% does not the structure of TS-1. 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. This is due to toluene will cover the catalyst surface, leaving lesser hydrogen peroxide on the catalyst surface. The formation of benzaldehyde which requires twice amount of hydrogen peroxide than the formation of cresol, therefore, decreases. The formation of cresols which requires lower hydrogen peroxide concentration on the catalyst surface, therefore, increases. The experimental results also show that the addition of Co into TS-1 suppresses the formation of benzaldehyde and increases the selectivity toward cresols. Too much Co added, however, will decrease the catalytic activity of the modified catalysts.

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

INTRODUCTION

Cresols are an organic compound which is widely used in several manufacture processes such as synthesis resins, to dissolve other chemical or used as insecticides. Cresol solutions are used as household cleaners and disinfectants. Cresols are important chemical raw material. They were originally obtained only from coal tar; after World War II, they were also obtained from spent refinery caustic. Since the mid-1960s, they have been produced synthetically on an increasingly large scale so called “Synthetic cresol”. 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 (2) the methanol alkylation of phenol process to produce cresol. The proposed route uses H_2O_2 as the oxidant and titanium silicalite-1 (TS-1) as the catalyst. This route is presents in **Figure 1.1**

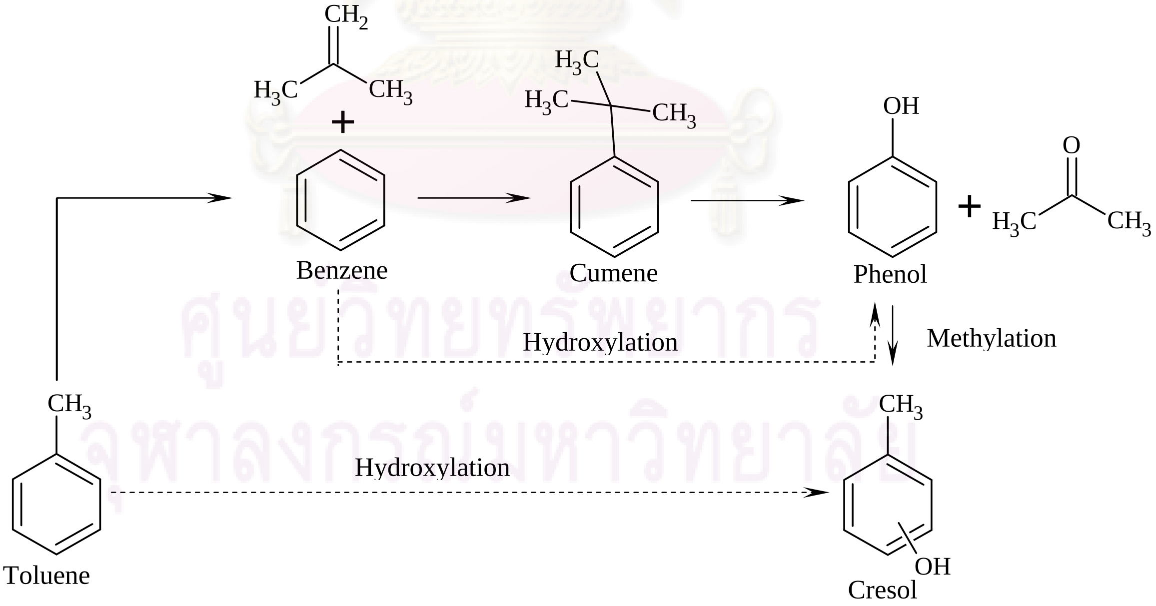


Figure 1.1 Routes to produce cresol.

Tatanium silicalite-1 (commonly know in the name TS-1) firstly revealed by Taramasso et al., 1983 was found to be an effective catalyst for the hydroxylation of benzene to phenol. Many researchers have applied this catalyst to several reactions such as hydroxylation of aromtics (Wu et al., 1998), the hydroxylation of bnzene to phenol (Wilkenhoner et al. and Perego et al., 2001), the propylene epoxidation (Wang et al., 2003) and the oxidation of aromatics (Bianchi et al., 2007)

The oxidation using H_2O_2 over TS-1 can occur at a relative low temperature (i.e. 70-80°C). Although, TS-1 has unique catalytic properties at low temperature but its still has low selectivity. Many researchers have studied several methods to improve the selectivity of this catalyst. For example, Pirutko et al. (2001) had study the second metal to modify the catalytic activity of TS-1 by adding Al, V, Cr, Fe, Co and Ru. They found Fe-TS-1 can catalyze the oxidation of benzene to phenol with high activity and selectivity. Poompichate (2005) had synthesized modified TS-1 by adding Cu, Co, Cr and V during the synthesis step. The results indicate that the second metal ions and titanium ion can simultaneously and homogeneously is incorporated into the framework of TS-1. In 2007, Kasemsiri had study 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 in the slurry reactor. The results show that all samples can be produced cresol but the Co-TS-1 has the maximum selectivity of cresol. At the same time, Jiang et al. (2008) modified TS-1 by adding Co for epoxidation of styrene by molecular oxygen. They found that Co loading has an importance effect on the catalytic property. The increasing in Co loading, both the styrene conversion and the selectivity to styrene oxide increased drastically, and then level off.

The present work introduce a new route to produce cresols in an one step reaction via the hydroxylation of toluene with TS-1 unmodified and modified by adding Co with several ratio to improve the catalytic selectivity of the catalyst. All samples were prepared by static hydrothermal method. The reaction uses a stirred slurry reactor under triphase condition. The research has scope following as:

1) Preparation TS-1 and M-TS-1 (M = Co) catalysts which have 50 Si to Ti and 200, 150 and 50 for Si to Co ratio respectively by using the hydrothermal method.

2) Pretreatment of these catalysts with 5M HNO_3 solution.

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

- Determination of crystallinity and structure of catalysts by X-ray diffractometer (XRD).
- Determination of bulk composition of Si, Ti and M by X-ray fluorescence (XRF).
- Determination the surface area and pore volume by N_2 Adsorption based on BET method (BET).
- Determination of incorporation of Ti atoms as a framework element by IR Spectroscopy (IR).

4) Study the catalytic reactions in a stirred slurry reactor at various temperature and various molar ratio toluene/H_2O_2 to determine catalytic activity.

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 aromatics reaction and comments on previous works.

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

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

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

CHAPTER II

THOERY AND LITERATUER REVIEWED

2.1 Electrophilic aromatic 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"

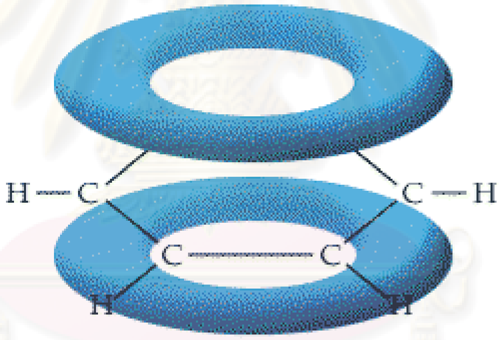


Figure 2.1 Electron cloud of benzene
(www.geocities.com/omegaman_uk/carbon.html)

Electrophilic aromatic substutition replaces a proton on benzene with another electrophile. Electrophilic aromatic substutition 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.

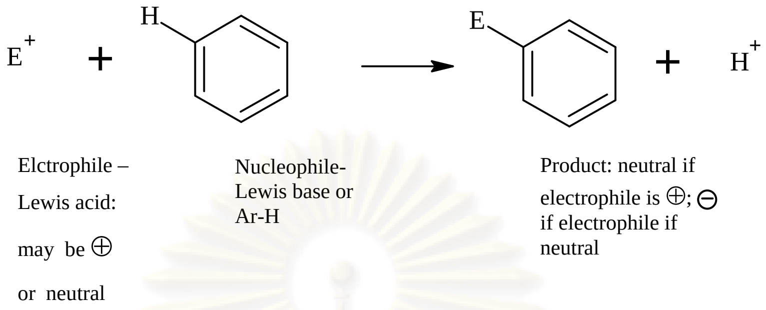


Figure 2.2 The mechanism of electrophilic aromatic substitution.

2.1.1 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

2.1.2 Theory of reactivity

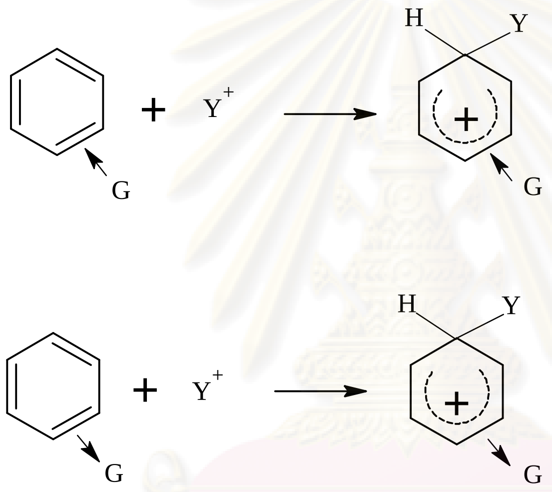
The activity of substituted benzene depends on type of substituent group. The group that releases electrons activates the ring is called “activating group”. The group that withdraws electrons deactivates the ring called “deactivating group”.

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 substutuents. The withdrawal of electrons from the ring destabilizes the positive charge that develops during the reaction, raising the energy of activation, and decreasing the reaction rate relative to benzene. **Figure 2.3** shows type of substituent group.



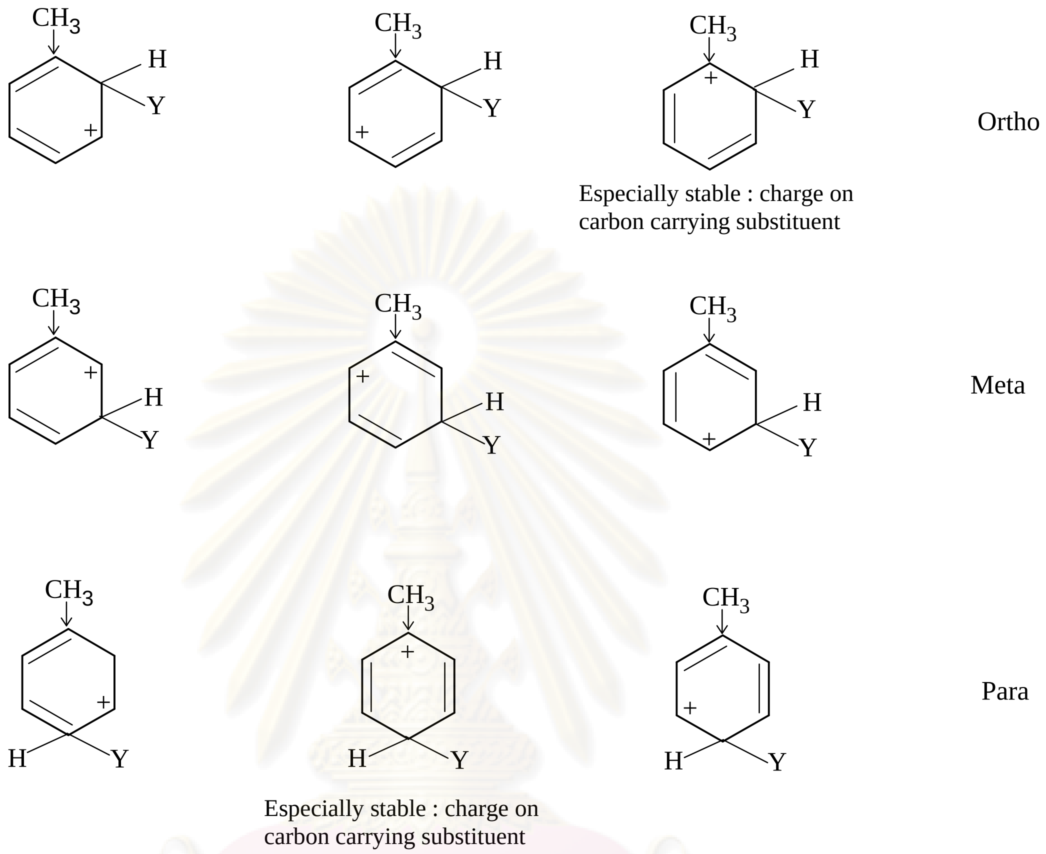
G = release electrons :
stabilizes carbocation,
activates

G = withdraws electrons :
destabilizes carbocation,
deactivates

Figure 2.3 Type of substituent group in electrophilic aromatic substitution

2.1.3 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 2.4** 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.

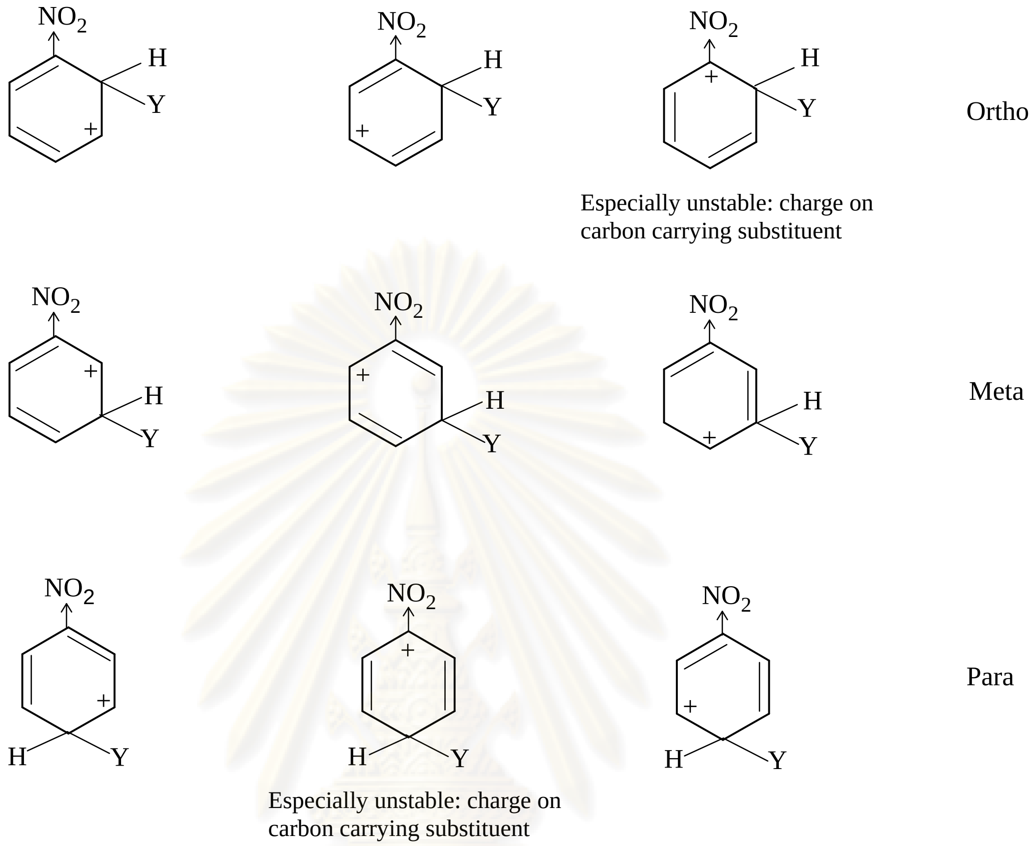


Especially stable : charge on carbon carrying substituent

Especially stable : charge on carbon carrying substituent

Figure 2.4 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 **Figure2.5**



Especially unstable: charge on carbon carrying substituent

Especially unstable: charge on carbon carrying substituent

Figure 2.5 Deactivating group substituent at position orho, para and meta.

2.2 Related literature review

The titanium silicalite was first synthesis by Taramasso et al. (1983). They found that TS-1 has a composition corresponding to the formula $xTiO_2(1-x)SiO_2$. 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 TS-1 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 method. The $Ti\text{-}O_2^-$ originated from framework titanium and H_2O_2 had the moderate stability and might be active site in an oxidation reaction. They found that TS-1 synthesized using TPABr as template did not contain anatase, but contained a kind of partly condensed titanium species with six-fold coordination. But, this kind of $Ti\text{-}O_2^-$ was very stable and could not be catalytic active site. Therefore, the six-fold coordination titanium species was suggested as be inactive in both the oxidation reaction and the decomposition of H_2O_2.

Titanium silicalite-1 was also used in various reactions such as oxidation, hydroxylation of aromatics Kumar et al. (1999) studies the hydroxylation of aromatics (such as benzene, toluene, anisole and benzyl chloride) over $TS\text{-}1/H_2O_2$ under triphase (solid-liquid-liquid) solvent free system and compared with biphase (solid-liquid) conditions in the presence of a co-solvent. They found that in case of benzyl chloride, triphase condition resulted in the ring hydroxylation forming *p*-hydroxy and *o*-hydroxy benzyl chloride (75%, *para:orho* ratio 85:15) along with side-chain oxyfuntionalization followed by HCl removal directly forming benzaldehyde (no formation of benzal chloride). The oxidation of cyclohexanone and acetophenone gave caprolactone and phenyl acetate, respectively, as major products (70-90% selectivity). The other hydroxyl-acetonphenones (acetonphenone) and they found that adding an amount of H_2SO_4 significantly increased the conversion.

Hulea and Dumitriu (2004) studied the styrene oxidation with H_2O_2 over Ti-containing molecular sieves with MFI, BEA and MCM-41 in liquid phase. They found that the catalytic activity expressed by TOF was found to be sequence in the order: Ti-beta > Ti-MCM-41 > TS-1. The main product of the styrene oxidation was styrene epoxide, phenylacetaldehyde, benzaldehyde and styrene glycol, but the product distribution depended on the nature of the catalyst. Thus, the selectivity to phenylacetaldehyde was very high for all catalysts of MFI type (smaller opening), whereas the benzaldehyde was form in large amount in the presence of Ti-beta and TiMCM-41 (large pores). Both the conversion of styrene and the selectivity towards phenylacetaldehyde increased with the reaction temperature. The nature of the solvent also influenced the catalytic activity and the selectivity to phenylacetaldehyde.

Some researchers try 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. Cumaranatunge and Delgass (2005) synthesized TS-1 modified by Au for propylene epoxidation. The Au/TS-1 still had pattern of MFI structure. The particle size range of Au was slightly above the 2-5 nm. Then, the catalysts were tested with propylene epoxidation. They found that higher Au loading (>0.1wt%), achived with the NH_4NO_3 treatment for this support, were determental to catalyst stability. Catalyst with Au loadings less than 0.1 wt% maintained a constant propylene oxide productivity, even after 12 h of reaction at 200ºC, whereas catalyst with Au loading of more than 0.1 wt% deactivated to about 80% of original activity. Catlysts with Au loading greater than 0.1 wt% have a higher number of Au particles compared with lower Au loading, and the increased proximity of sites could favor oligomerization of propylene oxide on the surface and thus led to catalyst deactivation.

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 and 95°C i.e. Co and V restrained benzaldehyde production while Al and Fe promoted the formation of benzaldehyde as main reaction product. In case of ethyl benzene hydroxylation at 70 and 95°C the predominant products were acetophenone and 1-phenethyl ethanol moreover Fe-TS-1 also has phenethyl alcohol and phenyl acetaldehyde. At the same time, Jiang et al. (2007) modified TS-1 by adding Co for epoxidation of styrene by molecular oxygen. XRD pattern showed all samples had MFI structure and did not exist of CoO_x crystalline peaks that indicated the CoO_x particles were not aggregated but highly dispersed on the surface of TS-1 and confirmed with DR UV-VIS which attributed to ultraviolet adsorbances of CoO_x oxide. Result of epoxidation of styrene to epoxide showed the Co loading has an important effect on the catalytic properties. With an increasing in the Co loading, both the styrene conversion and the selectivity to styrene oxide increased drastically, and then level off. When the Co loading increases continually, both the styrene conversion and the epoxide selectivity decreases markedly. The highest conversion was 94.5% and selectivity of epoxide was 74.3% with Co loading 2.32wt% and they found that there was a synergy between the Co and the Ti in the catalyst in the liquid phase epoxidation of styrene by O_2. This work prepared Co/TS-1 by immersion technique which is a complicate method, the preparation in a one step is therefore interesting.

From previous works, titanium silicalite-1 can improve the catalytic activity by adding the second metal for many reactions. Therefore, from research of Kasemsiri (2007) which use cobalt to improve the catalytic activity of TS-1 that point of interesting. The amount of metal loading has the limiting that should be investigate.

CHAPTER III

EXPERIMENTAL

The experimental in this chapter is divided into four 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, acidity of the catalyst characterised 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 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 97%	-	Aldrich
Tetrapropylammonium bromide 98%	-	Aldrich
Sodium chloride	Analytical	APS
Sodium hydroxide	Analytical	Merck
Sulfuric acid	Analytical	Aldrich
Sodium silicate solution	Extra pure	Merck
Cobalt(II)nitrate hexahydrate	Analytical	Aldrich
Toluene		
Hydrogen peroxide		
Ethanol		

3.1.2 Preparation procedures

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

Table 3.2 Reagents used for the preparation of Co-TS-1: Si/Ti = 50, Si/Co = 150*(Appendix A)

Solution for the gel preparation			Solution for decant-solution preparation		
Solution A1			Solution A2		
$Ti[O(CH_2)_3CH_3]_4$	2.2085	g	$Ti[O(CH_2)_3CH_3]_4$	2.2085	g
TPABr	5.72	g	TPABr	7.53	g
NaCl	11.95	g	De-ionized water	60	ml
$Co(NO_3)_2.6H_2O$	x	g	$Co(NO_3)_2.6H_2O$	x	g
De-ionized water	60	ml	H_2SO_4 (conc.)	3.4	ml
H_2SO_4 (conc.)	3.4	ml			
Solution B1			Solution B2		
Sodium silicate	69	g	Sodium silicate	69	g
De-ionized water	45	ml	De-ionized water	45	ml
Solution C1			Solution C2		
TPABr	2.16	g	NaCl	26.27	g
NaCl	40.59	g	De-ionized water	104	ml
NaOH	2.39	g			
De-ionized water	208	ml			
H_2SO_4 (conc.)	1.55	ml			

Si/Co =200, 150 and 50 respectively

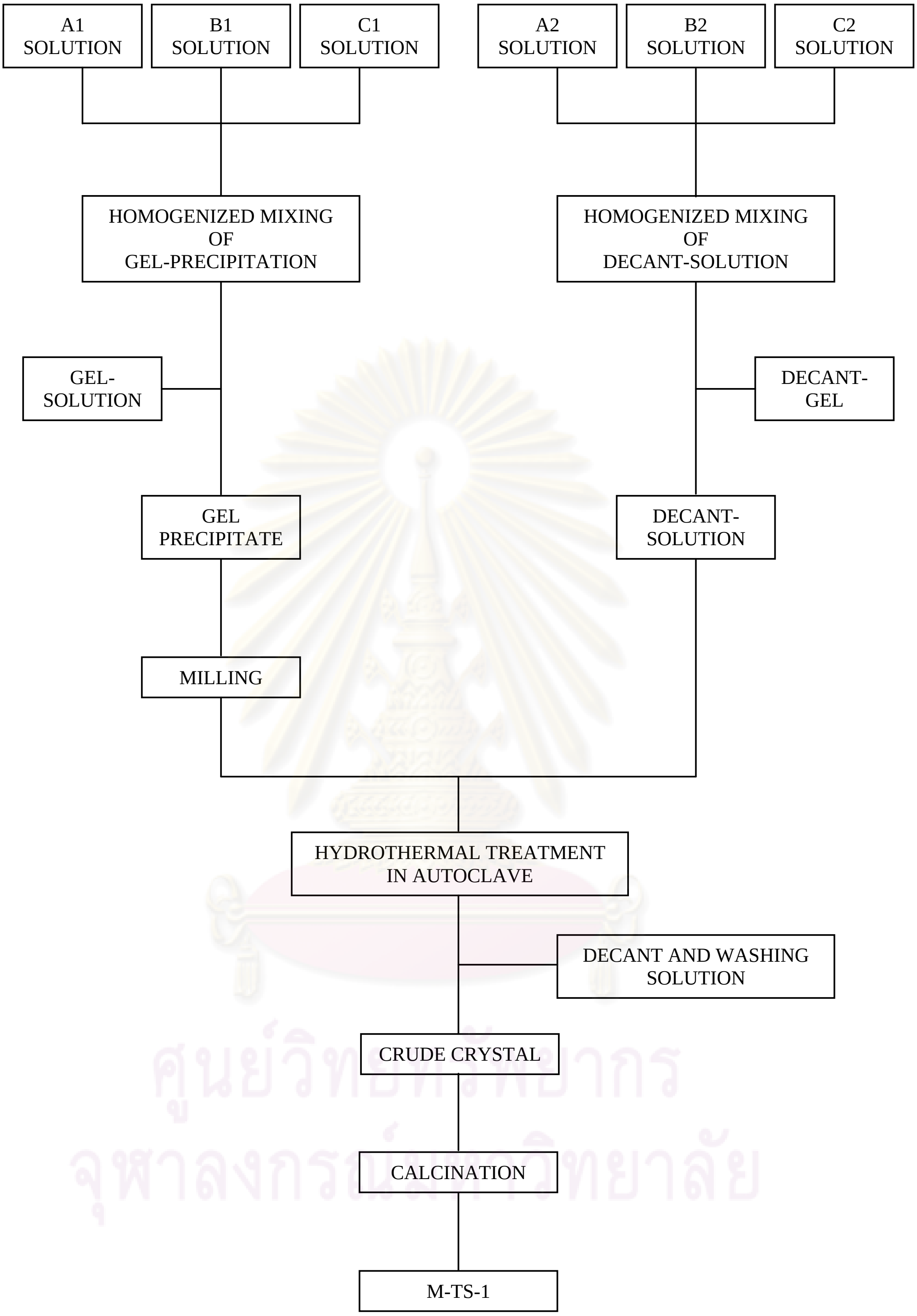


Figure 3.1 The preparation procedure of Co-TS-1 by hydrothermal method.

3.1.2.1 Preparation of gel precipitation and decantation Solution

The source of metals for preparation of decantation and gel solutions were $Co(NO_3)_2.6H_2O$ for Co, $Ti[O(CH_2)_3CH_3]_4$ for Ti, and sodium silicate for Si, respectively. TPABr (Tetra-n-propyl ammonium bromide $[(CH_3CH_2CH_2)_4N]Br$) was used as organic template. The atomic ratio of Silicon/Titanium set at 50 and Silicon/Co were set at 200, 150, and 50 respectively. The preparation of supernatant liquid was separated from the gel, which is important for preparing the uniform crystals. The detailed procedures were as follows: Firstly, a gel mixture was 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 was maintained within the range 9-11 because this pH range is suitable for precipitation. H_2SO_4 (conc.) or NaOH solution were used to adjust pH of the gel mixture to an appropriate level if it was necessary. After the addition,stirred gel mixture for 1 h, and was separated from supernatant liquid by centrifuge.

Secondly, a decantation solution was 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 were mixed together with the gel mixture. However, before mixing, the pH of solution was maintained between 9-11. The colorless supernatant liquid was separated from the mixture by centrifugation.

3.1.2.2 Crystallization

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

3.1.2.3 Calcination

The dry crystals were 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 of 8.6 ^{o}C/min, to burn off the organic template and leave the cavities and channels in the crystals. Then, the calcined crystals were finally cooled down to room temperature in a dessicator.

3.1.3 Treatment catalysts

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

3.2 Catalyst characterization

3.2.1 X-Ray Fluorescence Spectrometer (XRF)

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

3.2.2 BET surface area measurement

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

3.2.3 X-Ray Diffraction (XRD)

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

3.2.4 Fourier transform Infrared (FT-IR)

The functional group on the catalyst surface was determined by FT-IR using Nicolet model Impact 400. Each sample was mixed with KBr with ratio of sample: KBr equal to 1:100 and then pressed into a thin wafer. Infrared spectra were 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) was used to determine the acid properties of catalysts. NH_3-TPD was carried out using a flow apparatus. The catalyst sample (0.1 g) was treated at 550^{o}C in helium flow for 1h and then saturated with 15 %NH_3/He mixture after cooling to 80^{o}C. After purging with helium at 80^{o}C for 1 h to remove weakly physisorbed NH_3, the sample was heated to 550 ^{o}C at therate of 10^{o}C/min in a helium flow of 50 cm^{3}/min. The amount of acid sites on the catalyst surface was calculated from the desorption amount of NH_3. It was determined by measuring the areas of the desorption profiles obtained from the Micromeritics Chemisorb 2750 analyzer

The deconvlution of NH_3-TPD peak was carried out with the “fityk” curve fitting programme. The peaks were assumed to be Gaussian with showness shape (using parameter ‘SplitGaussian’ in the programme).

3.3 Reaction study in the hydroxylation of toluene

The hydroxylation of alkyl benzene (toluene) with H_2O_2 (30 wt% in water, Mecrk) was carried out in a 250 ml, paraffin oil jacketed, three-necked, glass flask fitted with a condenser and a mechanical stirrer placed in a stirring block heater as shown in **Figure 3.2.** The reaction was performed at atmospheric pressure. Typically, 1 g of a catalyst was reacted with reactant as toluene to H_2O_2 molar ratio equals to 1 to 1 and 50 ml of water. First, the catalyst and water using for dispersion of a catalyst were added into a reactor at 90°C for 1 h so as to drive out gases in pores of catalyst. Then reactant and H_2O_2 was added into reactor. For H_2O_2 was slowly injected drop-wise using a 1 ml syringe at 70ºC for 2 h. After the reaction has been stopped by cool down, 50 ml of ethanol was added into reactor to homogenize the aqueous phase and the organic phase. The products were analyzed by a gas chromatograph equipped with a FID detector (SHIMADZU GC9A).

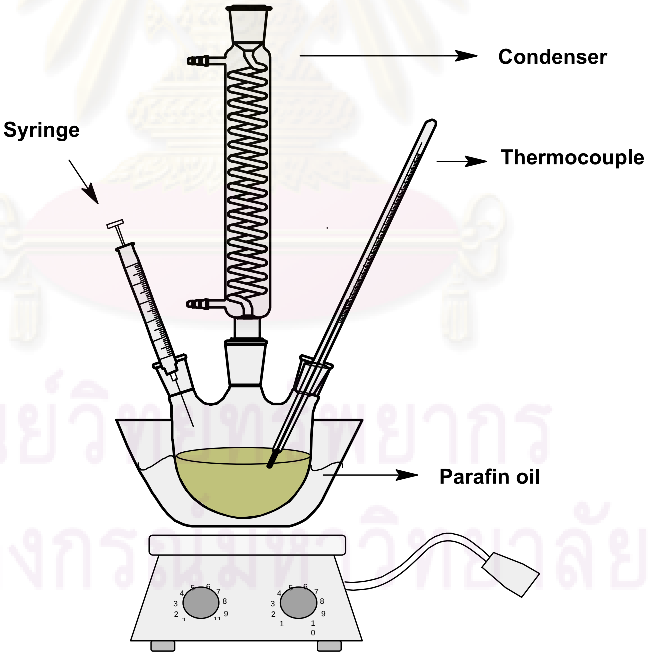


Figure 3.2 The hydroxylation reactor.

The operating conditions of the GC-9A is listed in **Table 3.3**

Table 3.3 Operating conditions for gas chromatograph

Gas chromatograph	SHIMADZU GC9A
Detector	FID
Packed column	GP 10% SP-2100
Column length (m)	
Carrier gas	N_2 (99.999%)
Carrier gas flow rate (ml/min)	30
Injector temperature (^oC)	250
Detector temperature (^oC)	250
Initial column temperature (^oC)	80
Programme rate (^oC/min)	2
Final column temperature (^oC)	240
Analyzed chemical samples	Toluene

CHAPTER IV

RESULTS AND DISCUSSION

This chapter is the results of catalyst characterization and catalytic performance evaluation. The following physical characteristics of catalysts; crystal structure (identified from XRD), location of titanium cation (determined from FT-IR), surface area (measured from BET technique), and catalyst composition (measured from XRF technique) are reported in section 4.1. Section 4.2 reports the catalytic activity of TS-1 and Co-TS-1 in the hydroxylation of toluene. The experimental results are presented as percentage of hydrogen peroxide convert to organic product, selectivity and yield of organic products.

In this study, TS-1 with 1 and 3 days hydrothermal aging are named TS-1(1) and TS-1(3) respectively. The names of TS-1 modified by adding different amount of Co with 3 days aging will be assigned after characterization by XRF technique.

4.1 Catalysts characteristics

4.1.1 Chemical compositions

The chemical compositions of TS-1 and Co-TS-1 are determined by X-Ray Fluorescence Spectrometer. The results are tabulated 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(1)	98.00	1.95	none	50.35	none
TS-1(3)	97.34	2.61	none	37.33	none
Co-TS-1(Si/Co=200)	97.50	2.30	0.165	42.45	590.9
Co-TS-1(Si/Co=150)	97.37	2.50	0.102	38.87	954.6
Co-TS-1(Si/Co=50)	98.07	1.74	0.124	56.23	790.9

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

The amount of cobalt added before crystallization and the amount of cobalt appeared in the obtained catalysts relate in an ambiguous manner. At low concentration of cobalt cation in the gel and decant solution, cobalt cations are further aparted. Therefore, cobalt cations have less chance to form a cobalt compound phase. Most of cobalt cations in the solutions, hence, are trapped in the MFI structure. This is possibly the explanation why Co-TS-1(Si/Co=200) has highest cobalt concentration in the MFI structure. From section 4.1.2 forward, Co-TS-1(Si/Co=200) will be named Co-TS-1(591). (The number “591” is the ratio of the obtained catalyst)

At a too high cobalt concentration in the gel and decant solutions, as in the case of Co-TS-1(Si/Co=150), cobalt cations may form a separate cobalt compound which is not a part of MFI structure and can be washed out by nitric acid solution during the treatment step. Because of this reason, the amount of cobalt appears in Co-TS-1(591) is lower than the amount of cobalt appears in Co-TS-1(Si/Co=200). From section 4.1.2 forward, Co-TS-1(Si/Co=150) will be name Co-TS-1(955).

If cobalt concentration in the gel and decant solutions further increased, the chance of cobalt cations incorporate into the MFI framework and the chance of cobalt cation to form its own cobalt compound(s) are both higher. The final concentration of cobalt in the obtained Co-TS-1 depends on which phenomenon has higher probability during the crystallization step. For example, Co-TS-1(Si/Co=50) is synthesized using cobalt nitrate 3 times higher than Co-TS-1(Si/Co=150), but the amount of cobalt appears in the structure of Co-TS-1(Si/Co=50) is only about 20% higher. This explains why when we further increase cobalt concentration in the solutions, the amount of cobalt appears in the obtained catalyst becomes increase again. From section 4.1.2 forward, Co-TS-1(Si/Co=50) will be name Co-TS-1(791).

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 recorded XRD patterns of TS-1 and TS-1 modified with Co (Co-TS-1) are summarized in **Figure 4.1**. All recorded XRD patterns show six main characteristic peaks at 2θ ≈ 8, 8.8, 14.8, 23.1, 24 and 26.7 which are typical for MFI structure (Taramasso et al., 1983), see Appendix G. The XRD pattern of cobalt oxide does not appeared in any obtained pattern.

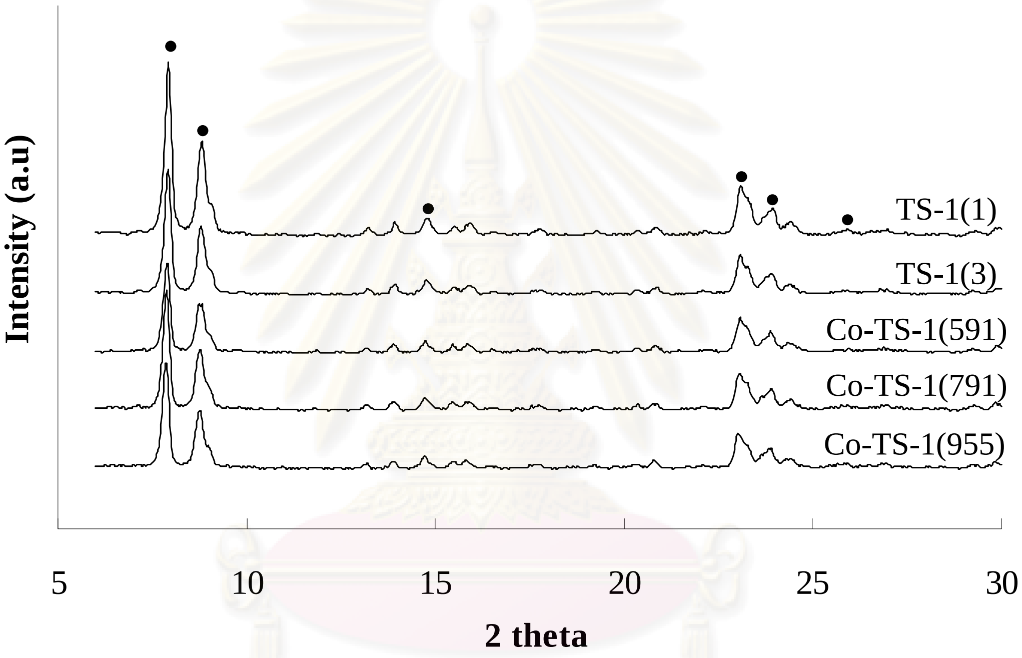


Figure 4.1 XRD patterns of TS-1 and Co-TS-1.

The appearance of the peaks at 2θ ≈ 24 and 26.7 indicates an orthorhombic symmetry which is typical for TS-1 having titanium cation (Ti^{4+}) within the framework of TS-1 having Si/Ti < 100 (Grienisen et al., 2000). The peaks at 2θ ≈ 24 and 26.7 are also interpreted as a change from a monoclinic symmetry (silicalite) (Taramasso et al., 1983) to a more catalytic active orthorhombic symmetry (Titanium silicalite). The absence of the peak at 2θ ≈ 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 synthesized using TPABr as the template (Li et al., 2001). These XRD patterns also show that adding cobalt up to 0.124 %mol does not destroy the structure of the catalyst.

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} 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)

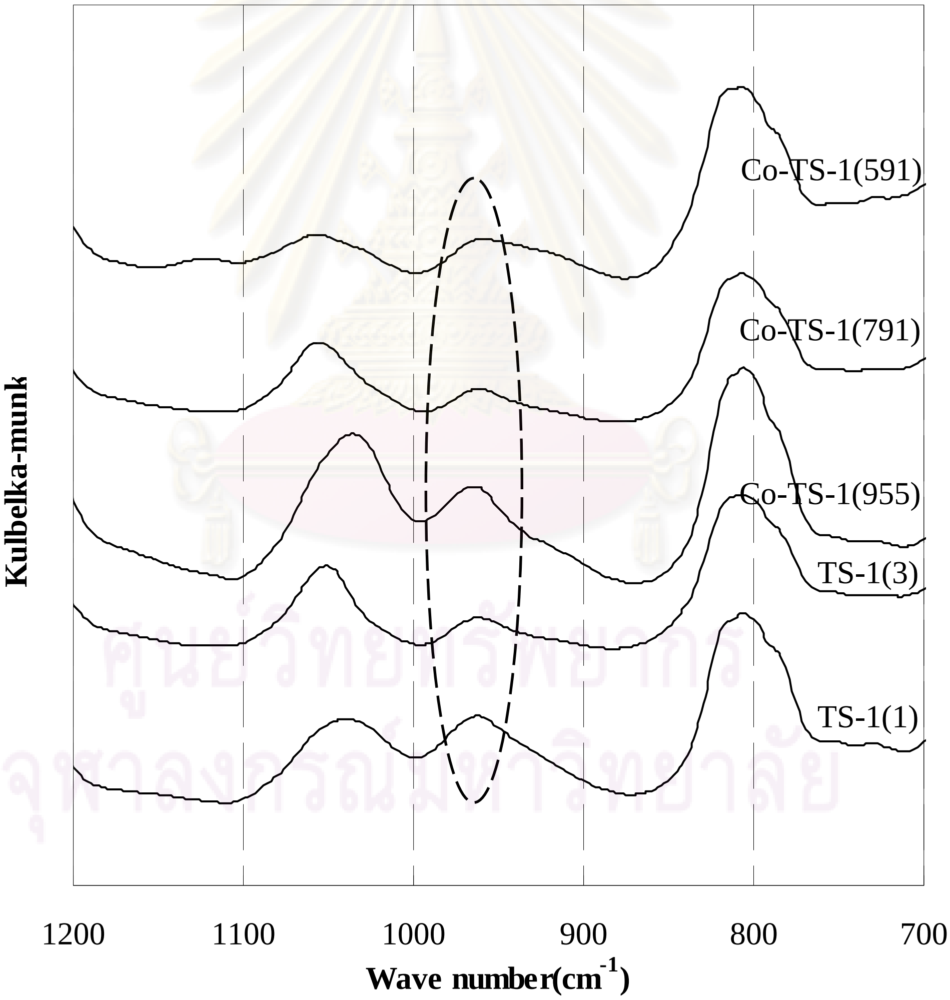


Figure 4.2 The absorption band of TS-1 and Co-TS-1 in wave number range between 700 – 1200 cm^{-1}

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 304-344 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	Surface area (m^2/g)
TS-1(1)	341
TS-1(3)	344
Co-TS-1(591)	304
Co-TS-1(791)	306
Co-TS-1(955)	338

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 hydroxylation of toluene with H_2O_2 as oxidant. This reaction produces mainly three products: benzaldehyde, ortho-cresol and para-cresol. But in this research the satisfied products are ortho-cresol (o-cresol) and para-cresol (p-cresol).

The experimental results are reported in the form of the total percent of converted hydrogen peroxide to organic products and mole of each product formed. In this research, effect of temperature and effect of molar ratio of toluene/H_2O_2, and effect of cobalt loading were investigated.

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

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

(b) Toluene will dissolve into the 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**

Toluene will dissolve into the bulk water phase. Then, the dissolved toluene in the bulk water phase diffuses into the water phase filled in the pores of the catalyst particle.

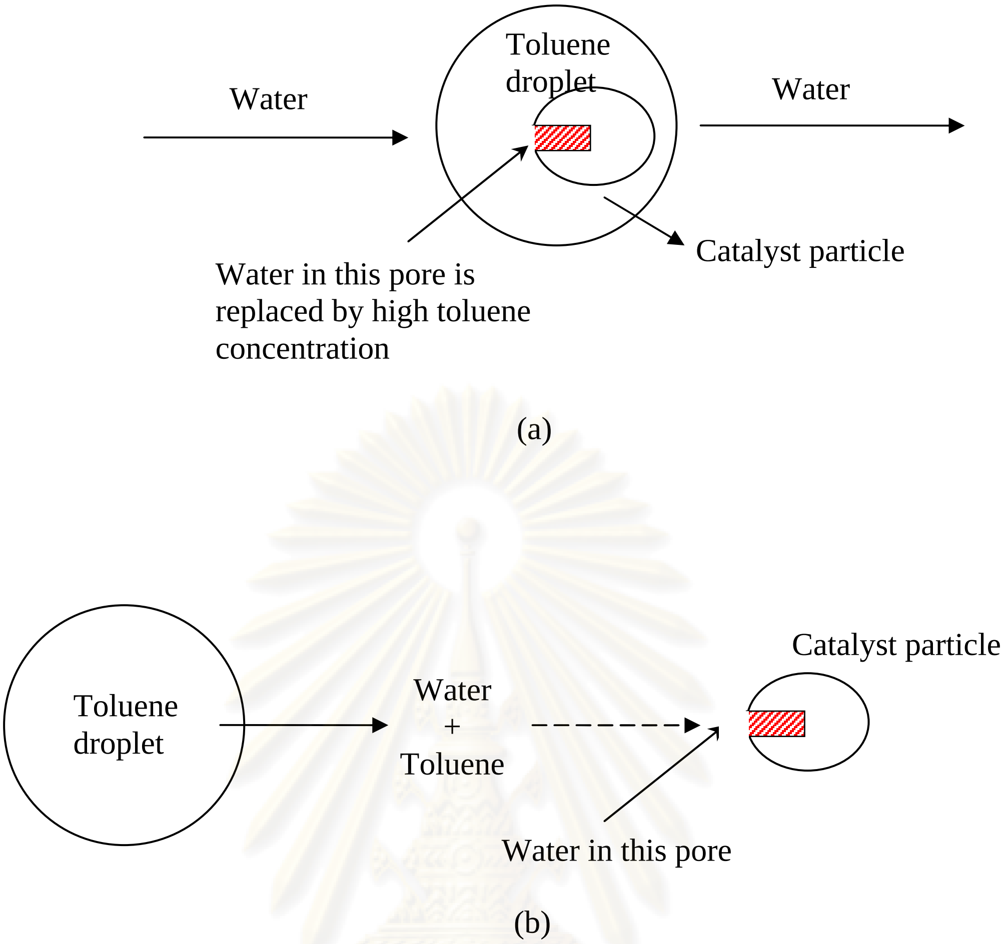


Figure 4.3 The phenomena during toluene contact with catalyst particle.

(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.

It should be noted here that “one” mole of H_2O_2 is required to produce one mole of cresol while “two” mole of H_2O_2 is required to produce one mole of benzaldehyde. Therefore, it is hypothesized that the molar ratio between H_2O_2 on the catalyst surface may take part in controlling which products should occur.

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

The first parameter affecting the reaction to be discussed is the molar ratio between toluene and H_2O_2. The effect of molar ratio of reactants (toluene/H_2O_2) on the % H_2O_2 converted to products obtained at the reaction temperature 70°C are illustrated in **Figures 4.4** and **4.5**. **Figure 4.4** shows the % H_2O_2 converted to products and **Figure 4.5** shows the product selectivity. It is observed that increasing the ratio toluene/H_2O_2 from 1:1 to 2:1 results in decreasing H_2O_2 conversion.

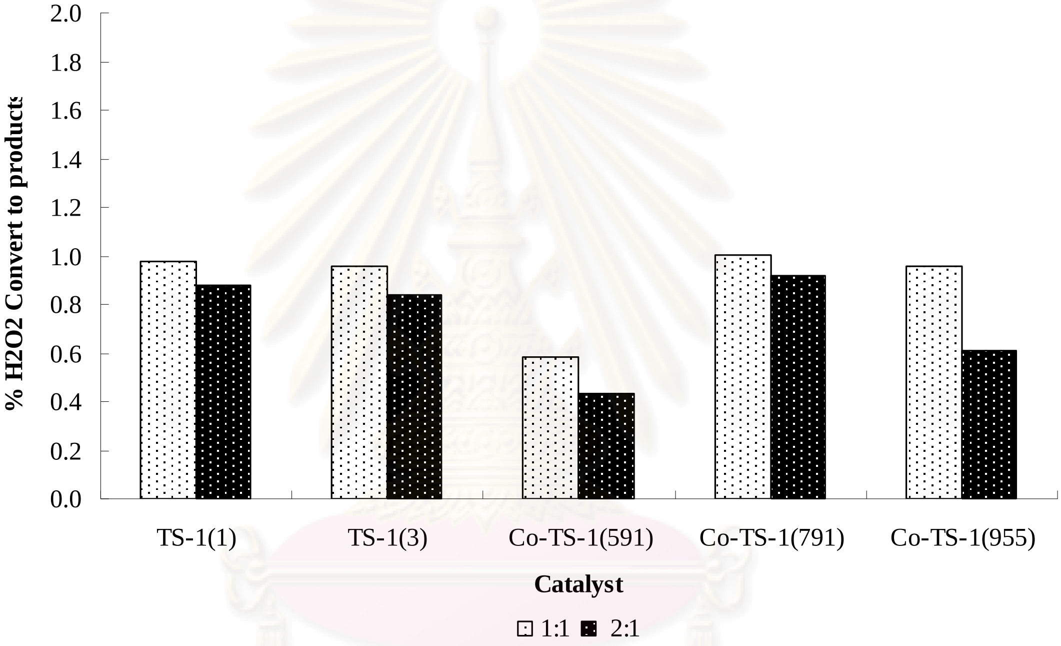


Figure 4.4 Percentage of H_2O_2 converts to product at 70ºC.

The observed decrease in H_2O_2 conversion of all catalysts should not be interpreted as the catalyst deactivation. Productivities of organic products (benzaldehyde, o-cresol, and p-cresol) of each catalyst showed in **Figure 4.5** illustrate the decrease in benzaldehyde production of all catalyst when the ratio of toluene/H_2O_2 is increased. Especially, TS-1(3) and Co-TS-1(791) show a pronounce suppression of benzaldehyde formation. For example, the productivity of benzaldehyde decreases from 5.838×10^-9 mol/sec to 4.0437×10^-10 mol/sec which is about 93% for TS-1(3) and from 5.402×10^-9 mol/sec to 2.371×10^-9 mol/sec which is about 56% for Co-TS-1(791).

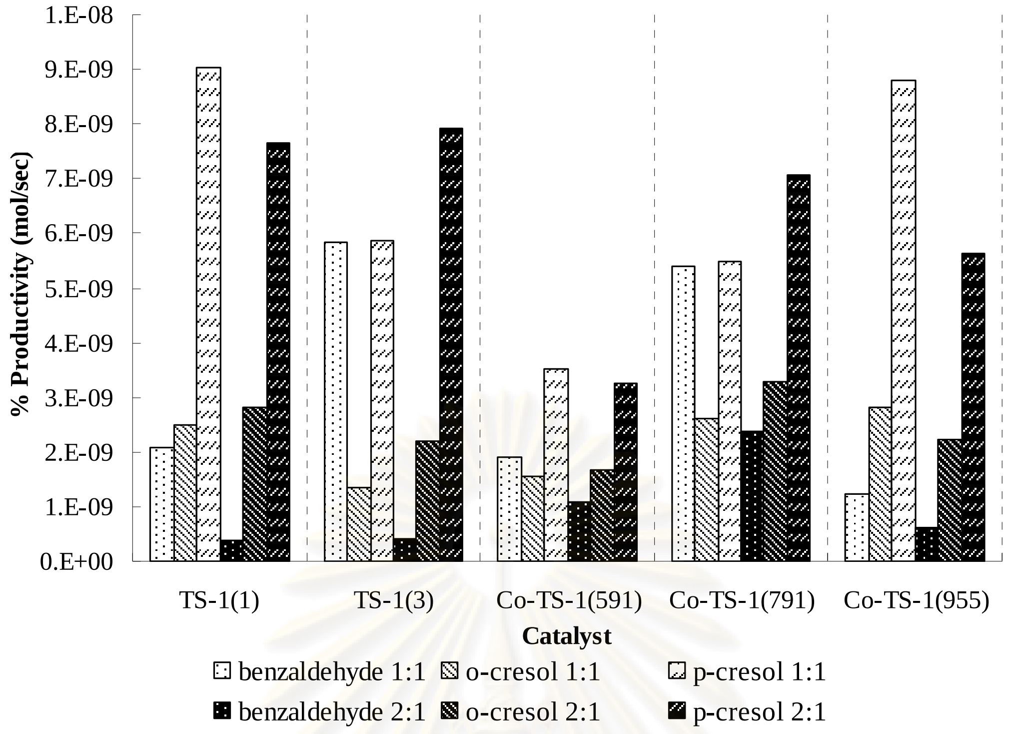


Figure 4.5 Productivity at 70ºC.

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

Figures 4.6 – 4.7 exhibits %H_2O_2 converted to organic products, and productivity respectively of the experimental results obtain from the reaction temperature 90°C. The behavior of p-cresol formation when toluene/H_2O_2 ratio is increase from 1:1 to 2:1 at this reaction temperature is the same as at 70°C, due to the same reason. The increasing of H_2O_2 conversion and the significantly increase in cresol selectivity is likely the effect of the behavior of water at temperature near its boiling point. It is known that the surface tension of water decreases when the water temperature increases. Water at 90°C has lower surface tension than at 70°C thus allowing more toluene to penetrate into the catalyst pore. The surface of the catalysts is, therefore, too rich in toluene and too lean in H_2O_2. This is the reason why the increasing of $\%H_2O_2$ convert to product and the increase in cresol selectivity is observed.

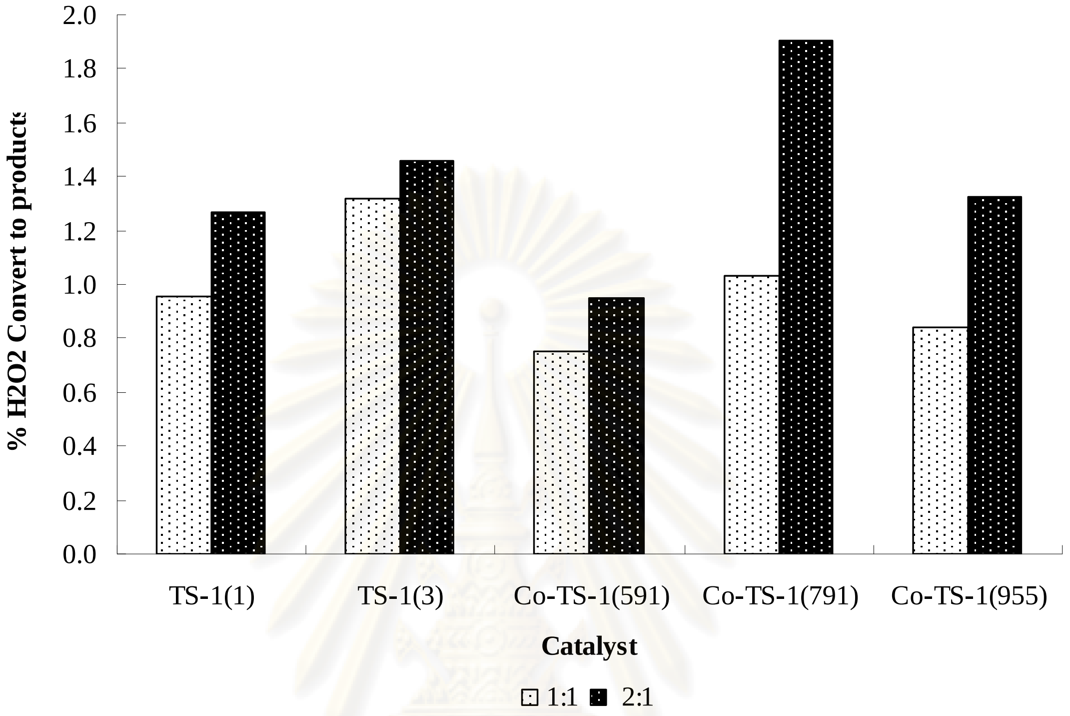


Figure 4.6 Percentage of H_2O_2 converts to product at 90 ºC.

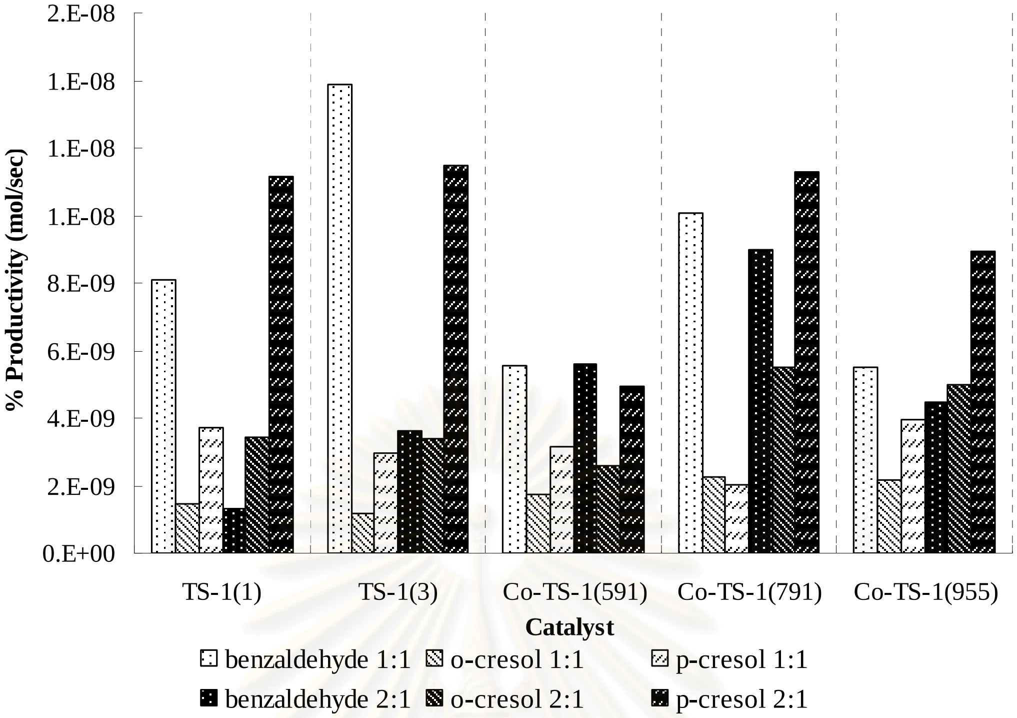


Figure 4.7 Productivity at 90ºC.

4.2.2 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 as previously described on page 26

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

Phenomenon a) will increase the hydroxylation rate of toluene to benzaldehyde while phenomenon b) will increase the selectivity to cresol as previously described in section 4.2.1 and demonstrated in Figures 4.6 and 4.7. For the hydroxylation reaction of toluene to cresol both phenomena produces contradicts effects. Phenomenon a) will increase the hydroxylation rate of toluene to benzaldehyde but phenomenon b) will increase the selectivity to cresol due to less H_2O_2 is available on the catalyst surface.

At the same toluene to H_2O_2 ratio, it is observed that when the reaction temperature is increased from 70ºC to 90ºC both the productivity and selectivity of benzaldehyde increase. This result suggests that phenomenon a) plays the major role. The results are illustrated in **Figures 4.8 – 4.10**

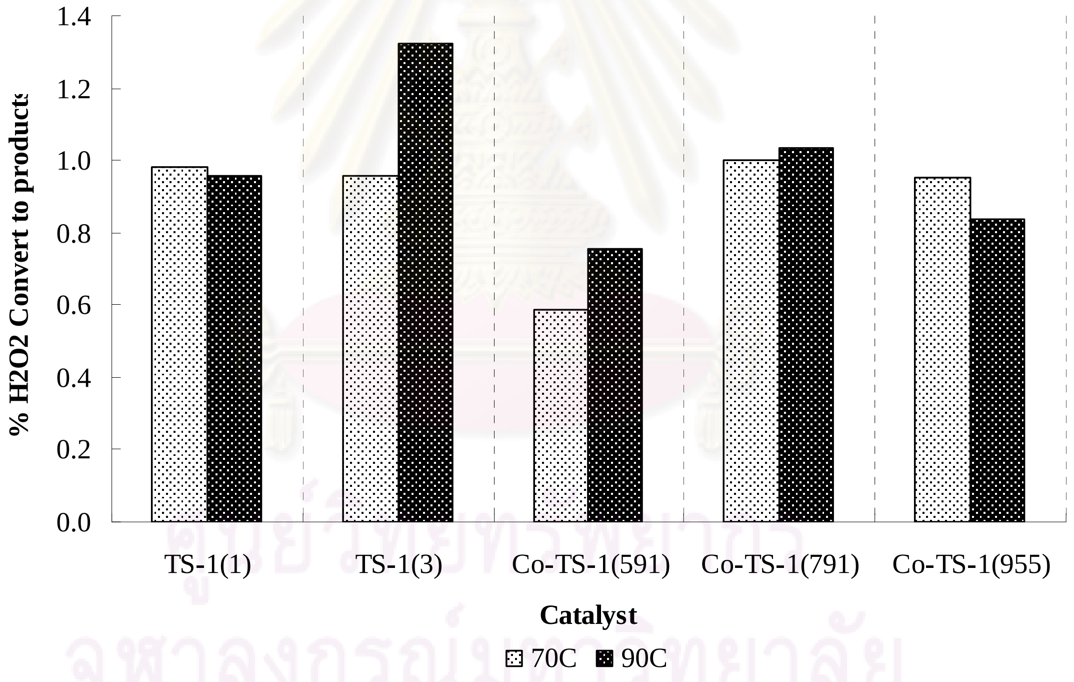


Figure 4.8 Percentage of H_2O_2 converts to product at molar ratio toluene/H_2O_2 = 1:1.

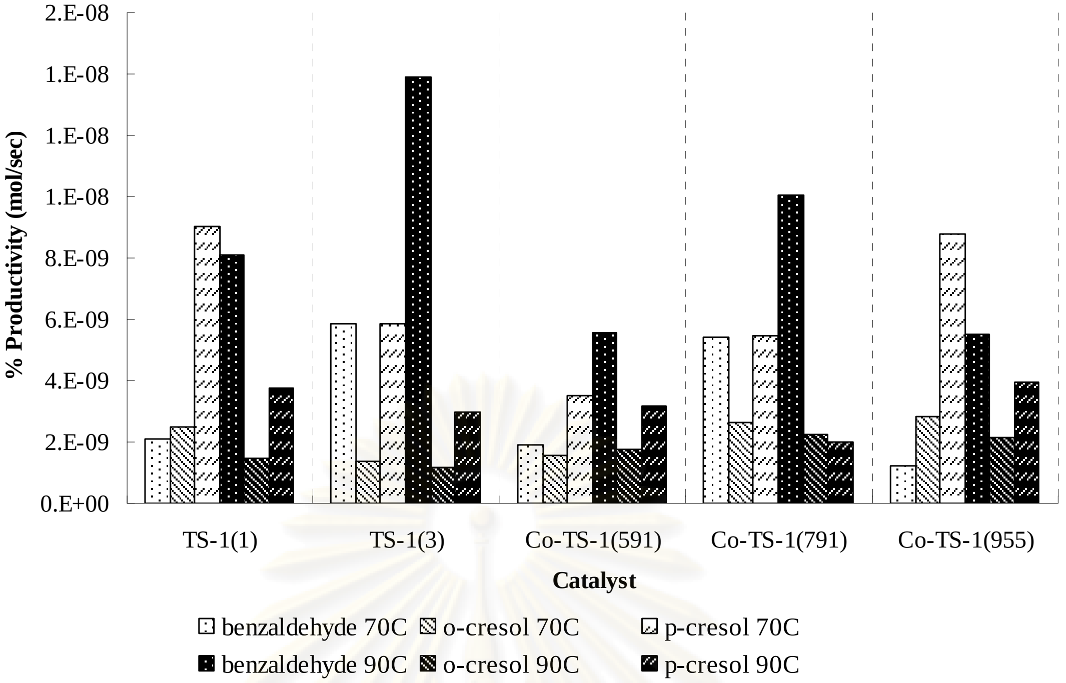


Figure 4.9 Productivity at molar ratio toluene/H_2O_2 = 1:1.

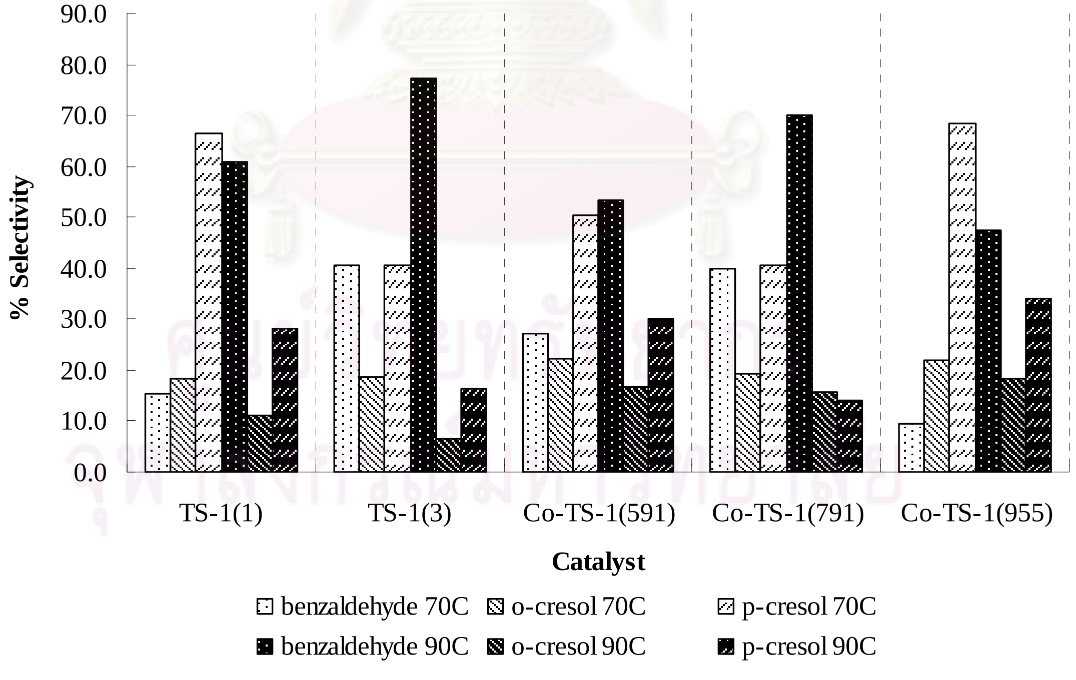


Figure 4.10 Product selectivity at molar ratio toluene/H_2O_2 = 1:1.

Let consider at the molar ratio toluene/H_2O_2 = 2:1, the productivity and product selectivity (as shown in **Figures 4.11** and **4.12)** are similar to the molar ratio toluene/H_2O_2 = 1:1. When the reaction temperature is increased, the productivity and selectivity of benzaldehyde increased. But as previously described in section 4.2.1 and showed in figure 4.10 that when toluene/H_2O_2 ratio is increased from 1:1 to 2:1, the catalyst surface is too rich in toluene and lack of H_2O_2. Therefore, cresols are allowed to produce more. Both benzaldehyde and cresols that are more produced causes % H_2O_2 converted to the organic products increase too (as shown in **Figure 4.13**).

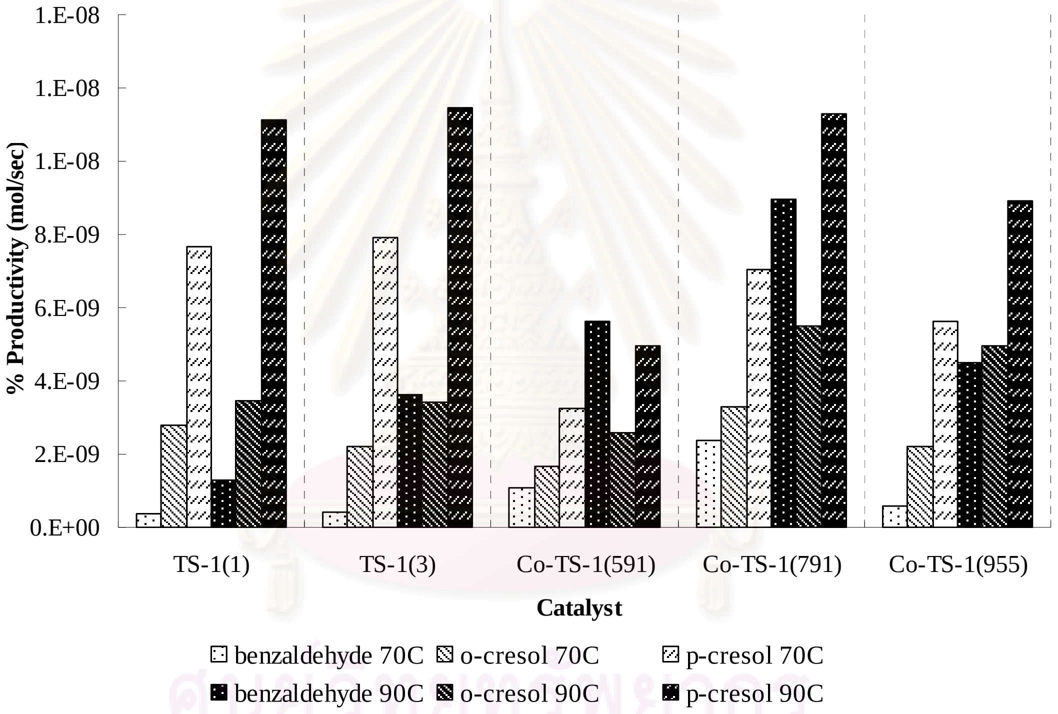


Figure 4.11 Productivity at molar ratio toluene/H_2O_2 = 2:1.

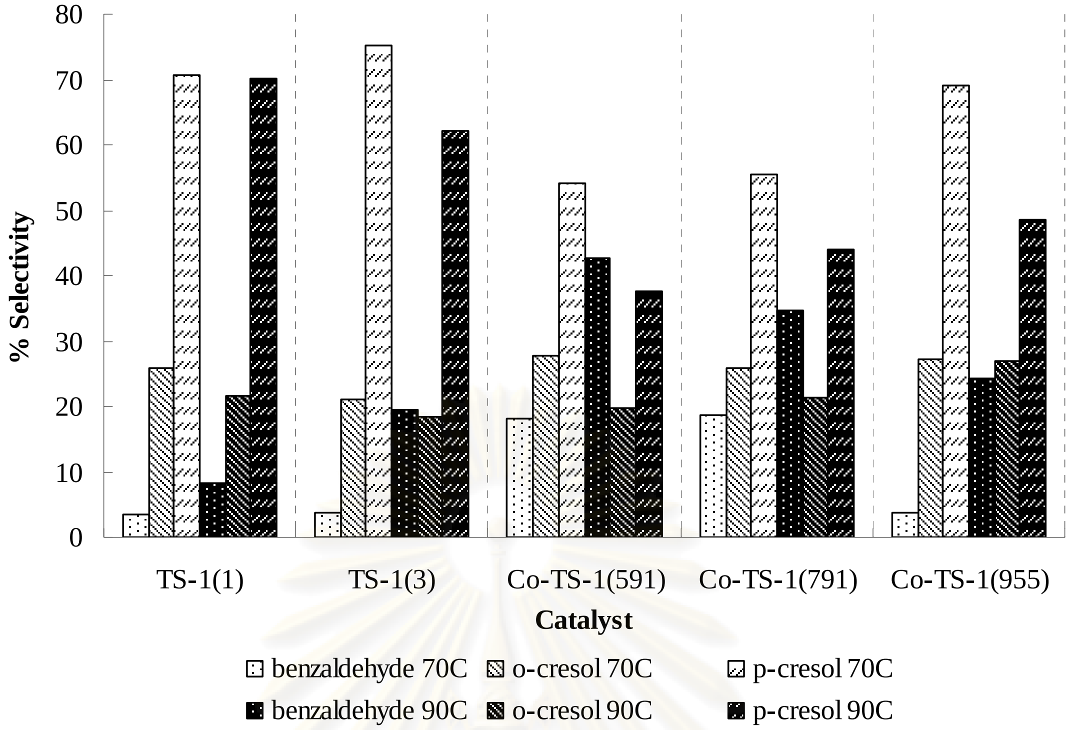


Figure 4.12 Product selectivity at molar ratio toluene/H_2O_2 = 2:1.

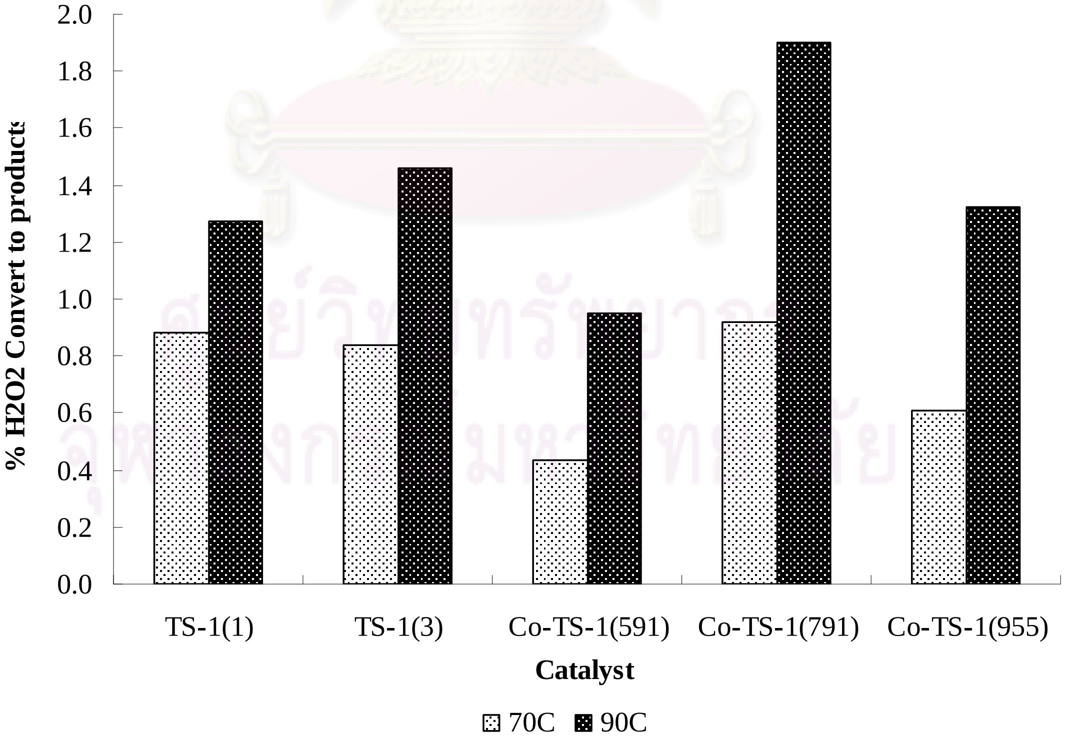


Figure 4.13 Percentage of H_2O_2 convert to product at molar ratio toluene/H_2O_2 = 2:1.

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 can be noticed at 70ºC with the molar ratio of toluene/H_2O_2 = 1:1 (see figure 4.8-4.10) that TS-(1) and Co-TS-1(955) have almost the same activity but the selectivity of combine cresols of Co-TS-1(955) is higher due to the formation of benzaldehyde is more suppressed on Co-TS-1(955) than TS-1(1).

Let consider the NH_3-TPD profiles, it is found that NH_3-TPD profiles of TS-1(1) and TS-1(3) can be deconvoluted into two main peaks. The first peak, will be named here "the weak acid site", appears around 130-137°C. The second peak, will be named here "the strong acid site", appears around 303 - 310°C. The profiles of TS-1(1) and TS-1(3) are showed in **Figures 4.14** and **4.15**. The NH_3-TPD of Co-TS-1(791), Co-TS-1(955), and Co-TS-1(591) are demonstrated in **Figures 4.16-4.18**. It is found that the NH_3-TPD profiles of Co-TS-1 can be deconvoluted into three peaks. They have a special peak which unmodified TS-1 does not exist that is the peak around 190 – 214°C which will be named here "the medium strength acid site". This peak possibly has effect on the catalytic activity of the catalysts.

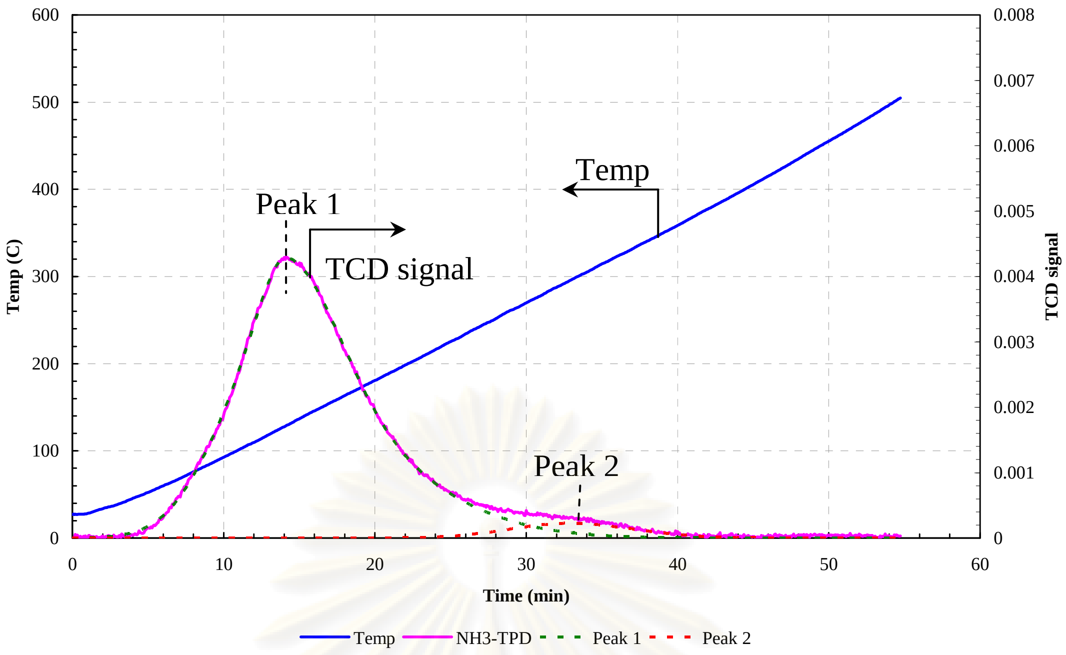


Figure 4.14 NH_3-TPD of TS-1(1).

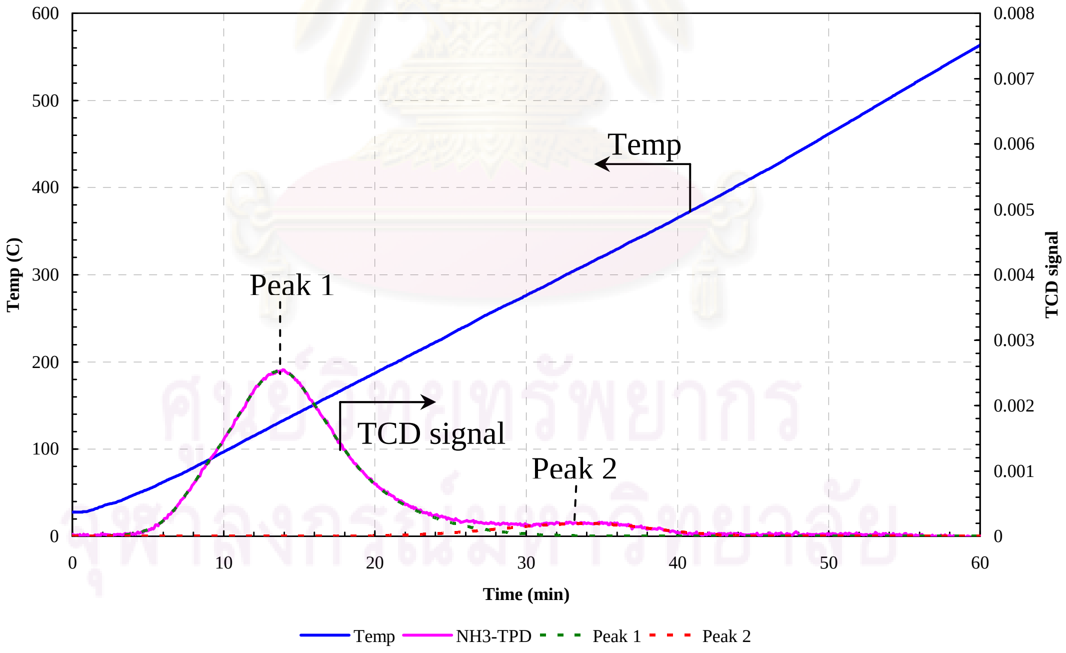


Figure 4.15 NH_3-TPD of TS-1(3).

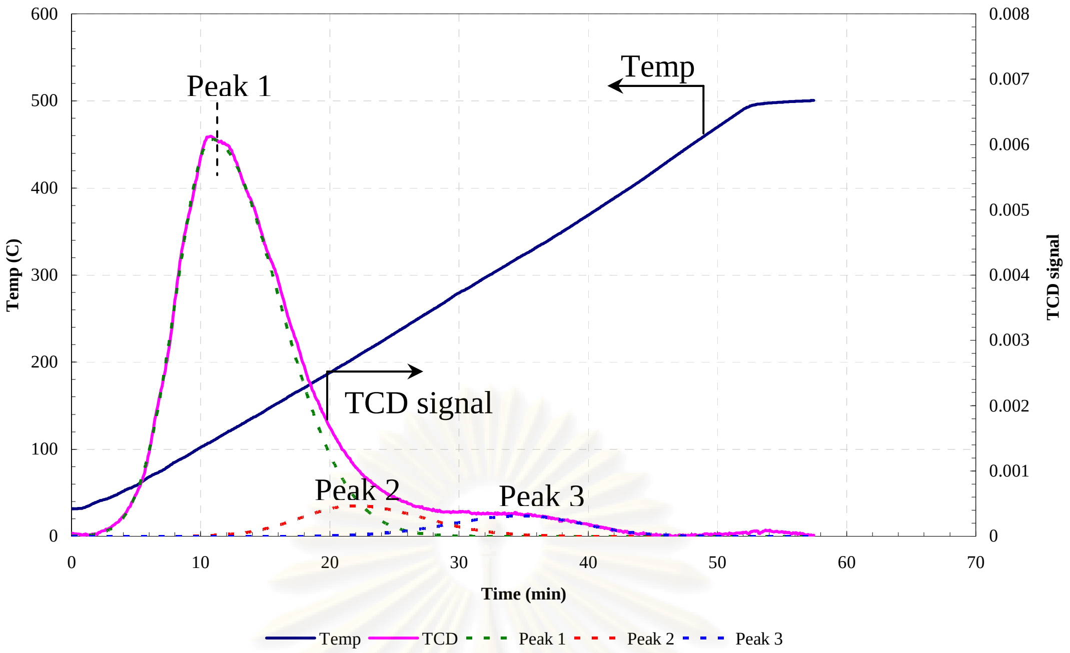


Figure 4.16 NH_3-TPD of Co-TS-1(591).

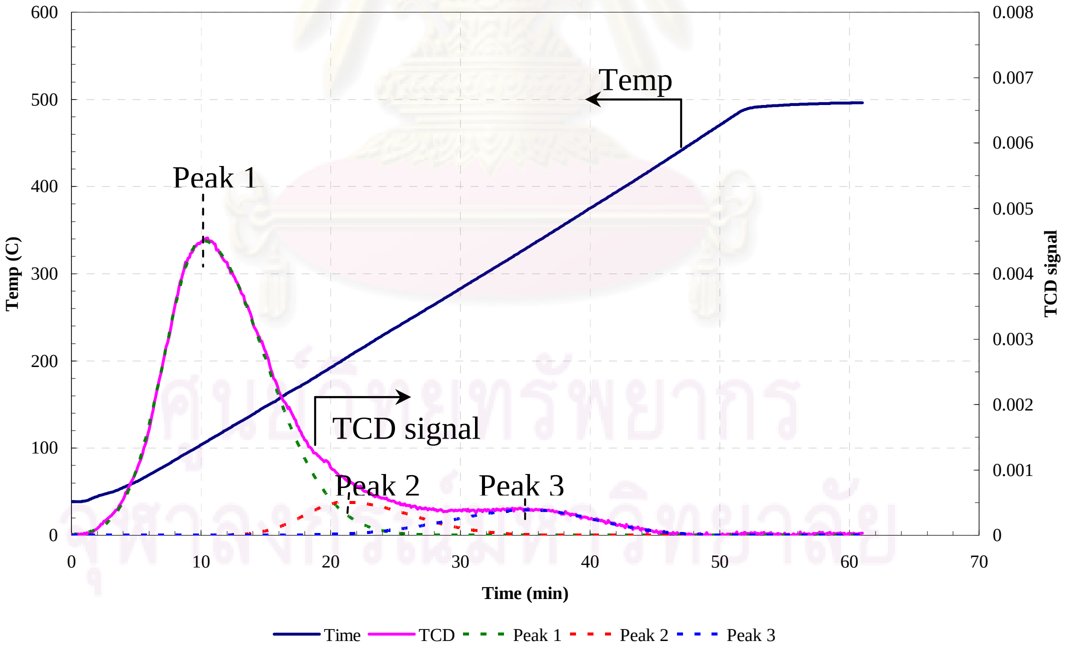


Figure 4.17 NH_3-TPD of Co-TS-1(791).

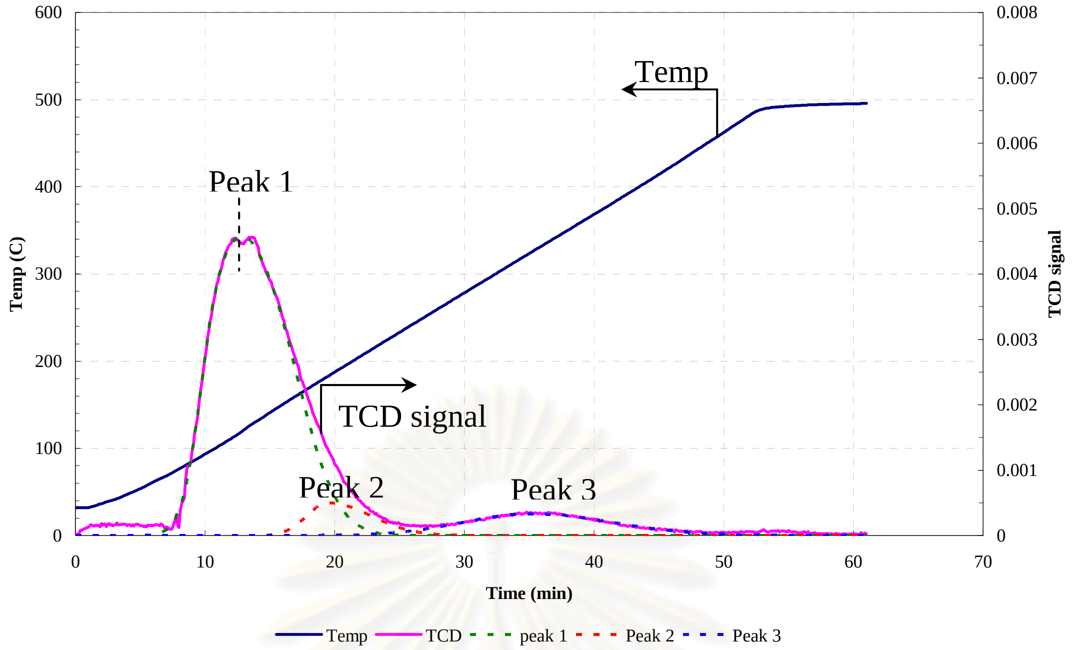


Figure 4.18 NH_3-TPD of Co-TS-1(955).

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

4.4.1 Proposed mechanism for the electrophilic substitution

It is generally known that the substitution position of the second group on the aromatic ring depends on the ability of the first substitution group to withdraw or supply electron to the ring. In case the first substitution group is an alkyl group (-CH_3 in case of toluene), the second substitution will prefer the ortho- or para- position. In our case, therefore, the appearance of o-cresol and p-cresol with the absence of m-cresol is not beyond expectation.

Let consider the results from the hydroxylation of toluene gives two parallel reactions that are the reaction occurs directly to benzene ring (4.1) and reaction on methyl group (4.2). The two parallel reactions are showed in **Figure 4.19**.

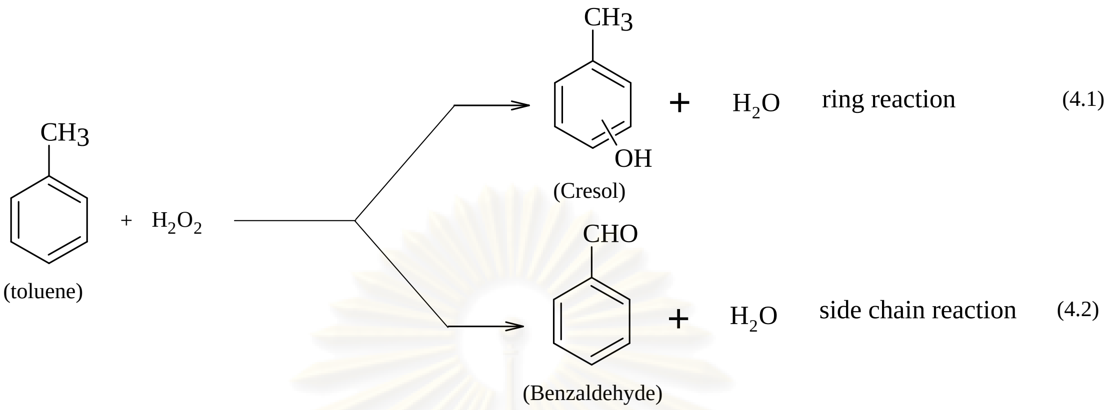


Figure 4.19 The two parallel reactions of hydroxylation of toluene.

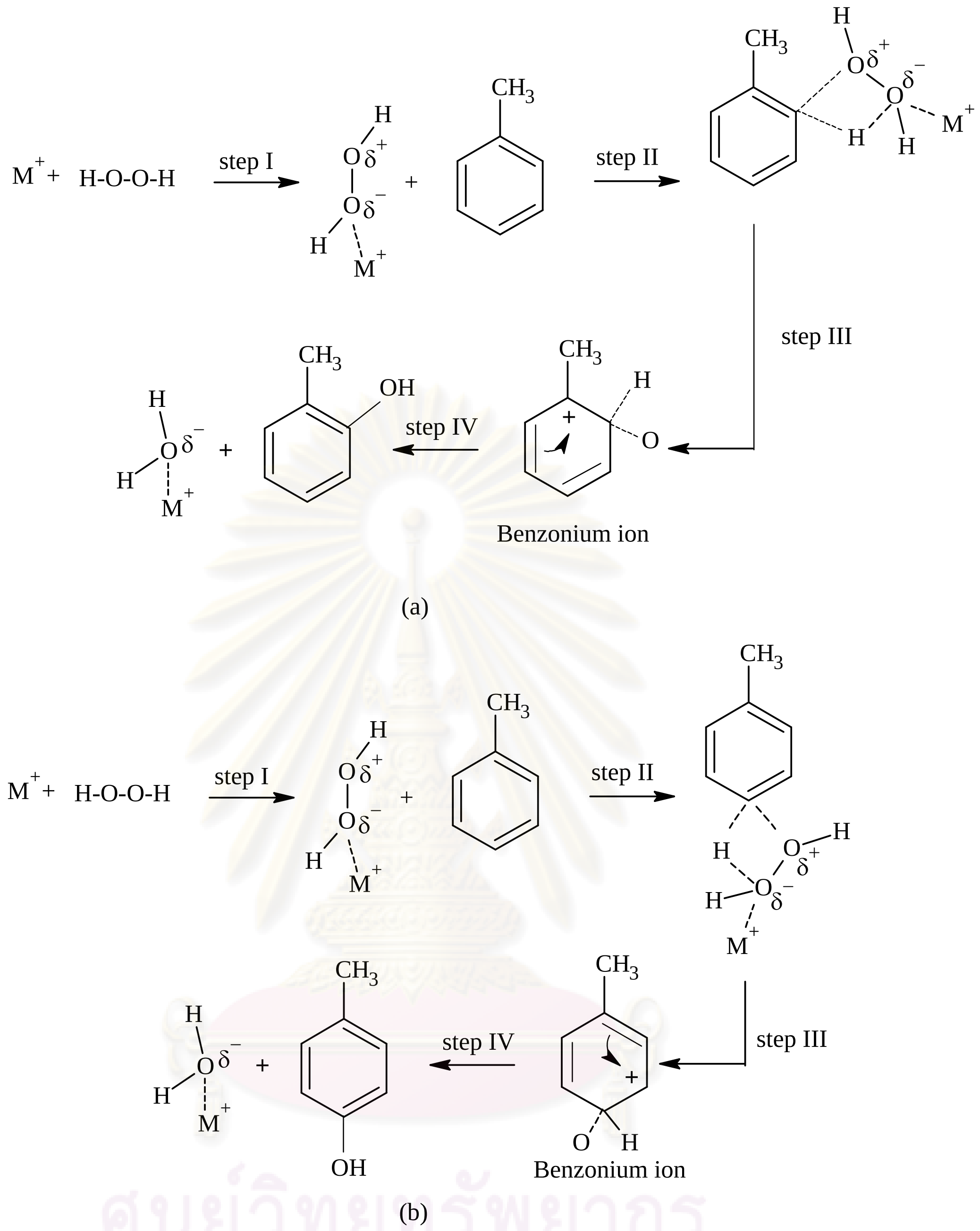
The mechanism for the formation of o-cresol and p-cresol are showed in **Figure 4.20**. The mechanism of cresol is proposed to consist of the following four steps:

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.



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

Figure 4.20 The mechanism of cresol in the hydroxylation of toluene o-cresol (a) and p-cresol (b).

4.4.2 Proposed mechanism for the oxidation at the methyl group

The reaction scheme of benzaldehyde formation is expected to be different from the mechanism of cresol formation. The hydrogen atoms of the alkyl group attached to the ring can be replaces by free radicals (such as H-O· and H-O-O·) more easily than hydrogen atom of the ring. Such free radicals may be generated from the decomposition of hydrogen peroxide by the presence of some cations. It is hypothesized that the formation of benzaldehyde will follow the mechanism similar to the halogenation of saturated hydrocarbon. The mechanism of the formation of benzaldehyde is showed in **Figure 4.21**. The active site in **Figure 4.21** is possibly the cations of Co and Ti which act as acidic site having strength higher than any other catalysts.

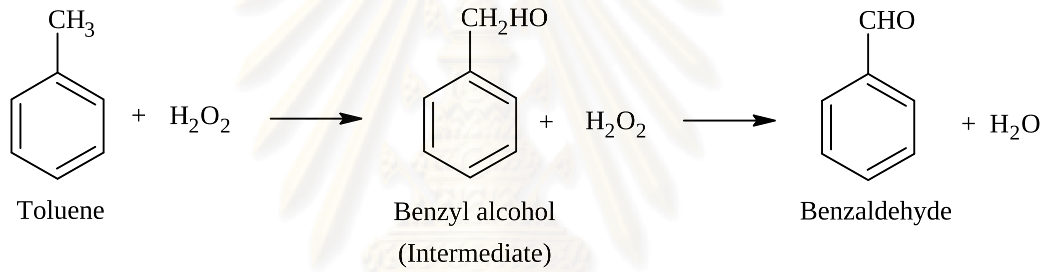


Figure 4.21 The reaction scheme of benzaldehyde formation**.**

4.5 Conclusions

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

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

In this study, the TS-1 and TS-1 modified with cabalt metal are prepared and investigated catalytic activity with the hydroxylation of toluene. The effect to catalytic activity due to molar ration toluene/H_2O_2, temperature and amount of cobalt loading 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

5.1 Summerization

The TS-1 and Co-TS-1 are synthesized by hydrothermal method. The cobalt metals are added incorporated during step of synthesis. All catalysts have the MFI structure with Ti^{4+} incorporated in the framework following normal characteristic of TS-1.and do not existing TiO_2 anatase phase. The amount of cobalt can be adding cobalt up to 0.124 %mol does not destroy the structure of the catalyst. The acid site of TS-1 can be organized into two group; i.e. weak acid site and strong acid site while Co-TS-1 can be organized into three groups; i.e. weak acid site, medium strength acid site and strong acid site.

The catalytic activity of toluene hydroxylation with effect of molar ratio of toluene/H_2O_2 is tested at 1:1 and 2:1, respectively. All catalysts give products as benzaldehyde, o-cresol, and p-cresol. At the same temperature as 70ºC, the benzaldehyde production decrease of all catalyst when the ratio of toluene/H_2O_2 is increased. The total % H_2O_2 convert to products follows order: Co-TS-1(791) > TS-1(1) > TS-1(3) > Co-TS-1(955) > Co-TS-1(591) and the selectivity of product observed follows sequence: Co-TS-1(955) > TS-1(1) > Co-TS-1(591) > Co-TS-1(791) > TS-1(3). When the temperature raise up produces an effect of the behavior of water at temperature near its boiling point. It is known that the surface tension of water decreases when the water temperature increases. Water at 90°C has lower surface tension than at 70°C thus allowing more toluene to penetrate into the catalyst pore. The surface of the catalysts is, therefore, too rich in toluene and too lean in H_2O_2 cause the increasing of %H_2O_2 convert to product and the increase in cresol selectivity.

An effect of temperature to hydroxylation of toluene, 70ºC and 90 ºC are investigated. At the same molar ratio of toluene/H_2O_2 as1:1, the reaction temperature is increased the productivity and selectivity of benzaldehyde increased due to reaction rate constant will increase following the Arrenius's equation. The total % H_2O_2 convert to products follows order: Co-TS-1(791) ≈ TS-1(1) ≈ Co-TS-1(955) ≈ TS-1(3) ≈ Co-TS-1(591) and the selectivity of product observed follows sequence: Co-TS-1(150) > TS-1(1) > Co-TS-1(591) > Co-TS-1(791) > TS-1(3). When the molar ratio of toluene/H_2O_2 increase the exhibit of productivity are similar at the molar ratio toluene/H_2O_2 = 1:1. The temperature increase combine with the molar ratio of toluene/H_2O_2 increase both of benzaldehyde and cresols that are more produced.

5.2 Recommendations

From the previous summerization, the following recommendations for future studies are proposed

(1) In this study, examine the catalystic activity of the catalyst at ambient pressure. It is possibly study at elevate pressure.

(2) 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.

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

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

$$= 0.3273$$

MFI catalyst

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

CALIBRATION CURVES

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

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

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

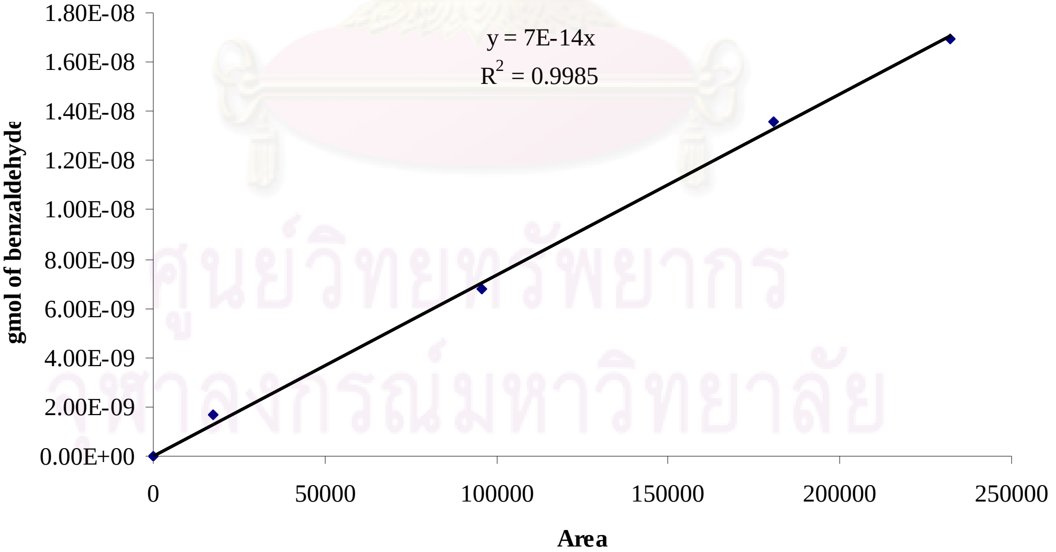


Figure B1 The calibration curve of benzaldehyde.

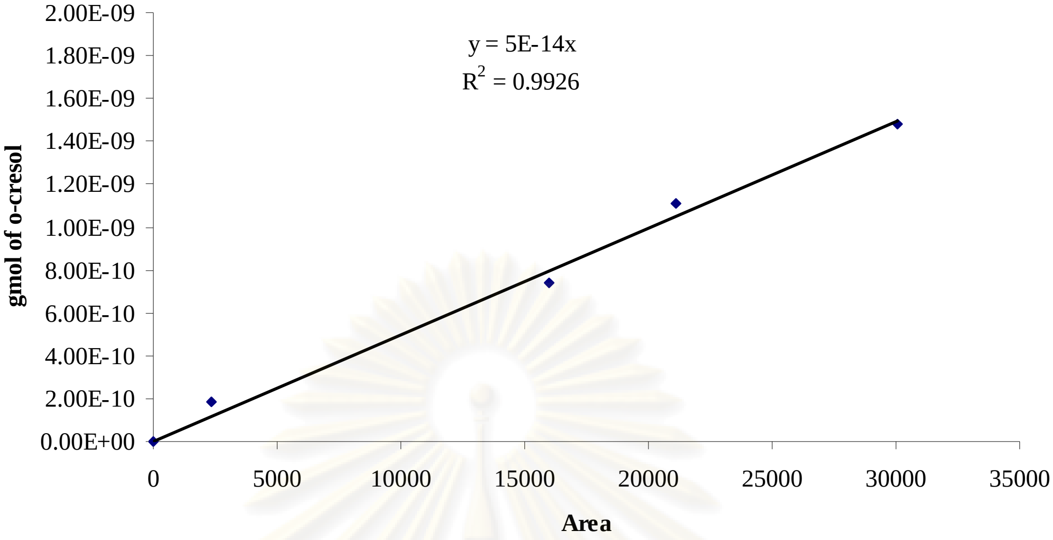


Figure B2 The calibration curve of o-cresol.

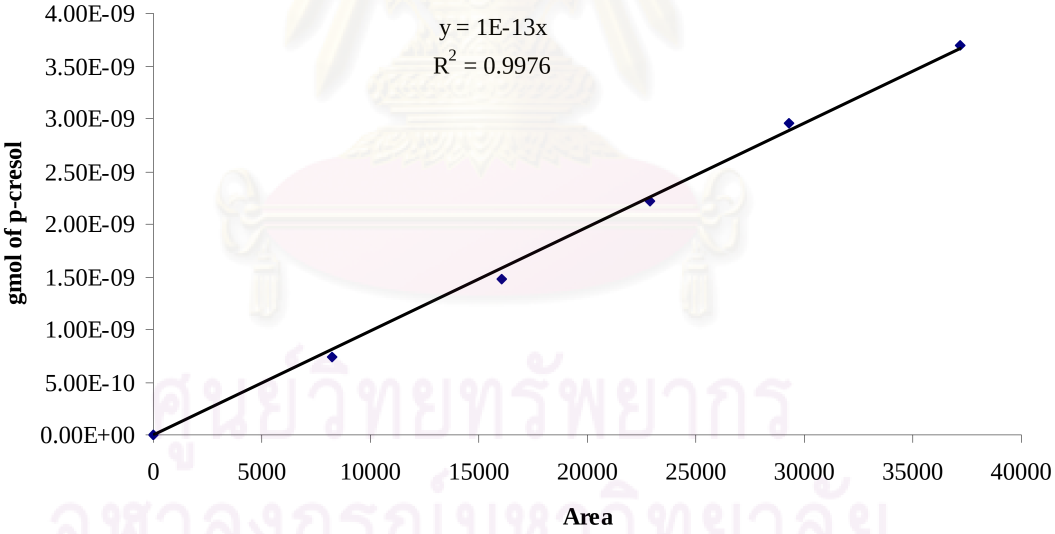


Figure B3 The calibration curve of p-cresol.

APPENDIX C

CALCULATION OF PRODUCTIVITY AND SECLECTIVITY

The productivity and selectivity for the hydroxylation of toluene was evaluated as example, selectivity and productivity of o-cresol

1. The productivity of o-cresol

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

2. The selectivity of product

$$\text{\% Selectivity of o-cresol} = \frac{\text{\% Conversion of toluene to cresol}}{\text{\% Total conversion of toluene to products}}$$

APPENDIX D

DATA OF EXPERIMENTS

Table D1 Data of Figure 4.8

Catalyst	% Total hydrogen peroxide convert to product at 70°C	
	Molar ratio toluene/H_2O_2	
	1:1	2:1
TS-1(1)	0.97980	0.87897
TS-1(3)	0.95910	0.83898
Co-TS-1(591)	0.58538	0.43399
Co-TS-1(791)	1.00276	0.91663
Co-TS-1(955)	0.95411	0.60892

Table D2 Data of Figure 4.9

Catalyst	Productivity at 70°C Molar ratio toluene/H_2O_2					
	1:1			2:1		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
TS-1(1)	2.083E-09	2.488E-09	9.024E-09	3.6707E-10	2.80168E-09	7.66588E-09
TS-1(3)	5.838E-09	1.35E-09	5.859E-09	4.0437E-10	2.20904E-09	7.91397E-09
Co-TS-1(591)	5.402E-09	2.617E-09	5.487E-09	2.371E-09	3.28639E-09	7.06081E-09
Co-TS-1(791)	1.9E-09	1.545E-09	3.522E-09	1.084E-09	1.67569E-09	3.26195E-09
Co-TS-1(955)	1.236E-09	2.821E-09	8.794E-09	6.0193E-10	2.21954E-09	5.62727E-09

Table D3 Data of Figure 4.10

Catalyst	% Total hydrogen peroxide convert to product at 90°C Molar ratio toluene/H_2O_2	
	1:1	2:1
TS-1(1)	0.9585	1.2706
TS-1(3)	1.3214	1.4588
Co-TS-1(591)	0.7544	0.9489
Co-TS-1(791)	1.0320	1.9037
Co-TS-1(955)	0.8384	1.3249

Table D4 Data of Figure 4.11

Catalyst	Productivity at 90°C Molar ratio toluene/H_2O_2					
	1:1			2:1		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
TS-1(1)	8.10E-09	1.47E-09	3.73E-09	1.31E-09	3.45E-09	1.11E-08
TS-1(3)	1.39E-08	1.18E-09	2.98E-09	3.61E-09	3.4E-09	1.15E-08
Co-TS-1(591)	1.01E-08	2.25E-09	2.02E-09	8.97E-09	5.5E-09	1.13E-08
Co-TS-1(791)	5.57E-09	1.73E-09	3.17E-09	5.61E-09	2.6E-09	4.95E-09
Co-TS-1(955)	5.51E-09	2.15E-09	3.97E-09	4.48E-09	4.97E-09	8.93E-09

Table D5 Data of Figure 4.12

Catalyst	% Total hydrogen peroxide convert to products at molar ratio of toluene/H_2O_2 = 1:1	
	At 70°C	At 90°C
TS-1(1)	0.97980	0.9585
TS-1(3)	0.95910	1.3214
Co-TS-1(591)	0.58538	0.7544
Co-TS-1(791)	1.00276	1.0320
Co-TS-1(955)	0.95411	0.8384

Table D6 Data of Figure 4.13

Catalyst	% Product selectivities at molar ratio of toluene/H_2O_2 = 1:1					
	At 70°C			At 90°C		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
TS-1(1)	2.08E-09	2.49E-09	9.02E-09	8.10E-09	1.47E-09	3.73E-09
TS-1(3)	5.84E-09	1.35E-09	5.86E-09	1.39E-08	1.18E-09	2.98E-09
Co-TS-1(591)	5.4E-09	2.62E-09	5.49E-09	1.01E-08	2.25E-09	2.02E-09
Co-TS-1(791)	1.9E-09	1.54E-09	3.52E-09	5.57E-09	1.73E-09	3.17E-09
Co-TS-1(955)	1.24E-09	2.82E-09	8.79E-09	5.51E-09	2.15E-09	3.97E-09

Table D7 Data of Figure 4.14

Catalyst	% Total hydrogen peroxide convert to products at molar ratio of toluene/H_2O_2 = 2:1	
	At 70°C	At 90°C
TS-1(1)	0.87897	1.2706
TS-1(3)	0.83898	1.4588
Co-TS-1(591)	0.43399	0.9489
Co-TS-1(791)	0.91663	1.9037
Co-TS-1(955)	0.60892	1.3249

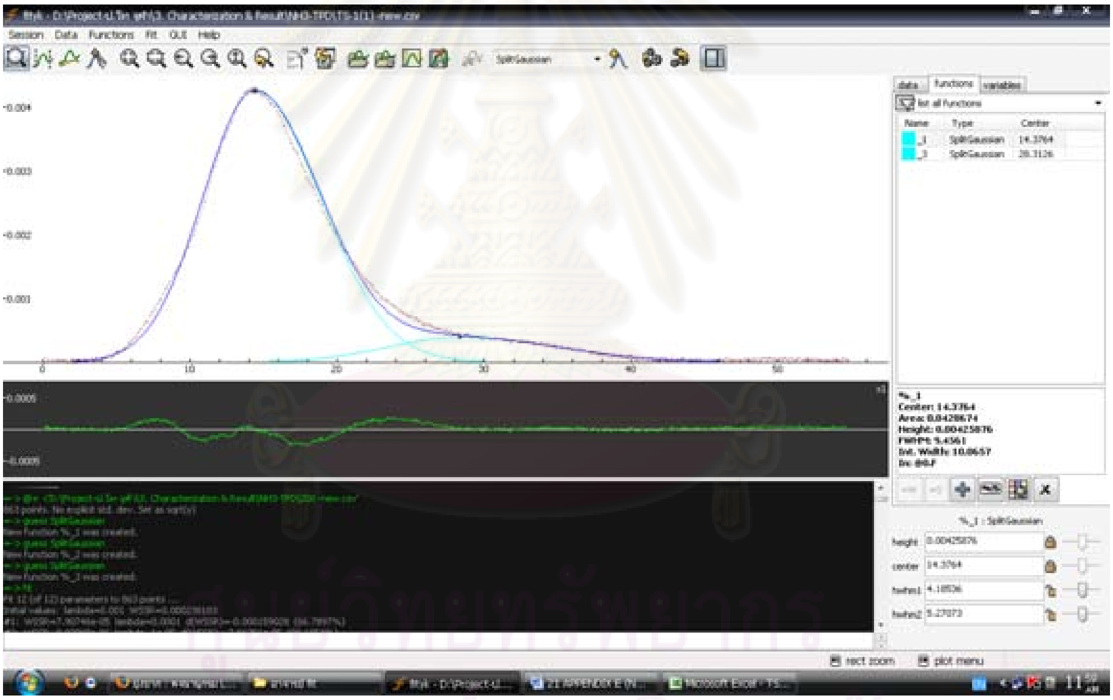
Table D8 Data of Figure 4.15

Catalyst	% Product selectivities at molar ratio of toluene/H_2O_2 = 2:1					
	At 70°C			At 90°C		
	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol
TS-1(1)	3.671E-10	2.802E-09	7.666E-09	1.308E-09	3.449E-09	1.114E-08
TS-1(3)	4.044E-10	2.209E-09	7.914E-09	3.606E-09	3.399E-09	1.148E-08
Co-TS-1(591)	2.371E-09	3.286E-09	7.061E-09	8.969E-09	5.505E-09	1.131E-08
Co-TS-1(791)	1.084E-09	1.676E-09	3.262E-09	5.614E-09	2.6E-09	4.952E-09
Co-TS-1(955)	6.019E-10	2.22E-09	5.627E-09	4.485E-09	4.968E-09	8.93E-09

APPENDIX E

NH_3-TPD

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 3 groups, according to their desorption peaks. The first one locates around 130-150 °C which will be named here “the weak acid site”. The second one locates around 150-180 °C which will be named here “the medium strength acid site” and the last group locates higher than 180 °C and will be named here “the strong acid site”. The location of each peak and amount of peak type of the acidic site



Name	Type	Center
_1	SplitGaussian	14.3764
_3	SplitGaussian	28.3126

%_1
Center: 14.3764
Area: 0.0428674
Height: 0.00425876
FWHM: 9.4561
Int. Width: 10.0657
In: @0.F

%_1 : SplitGaussian

height 0.00425876
center 14.3764
hwhm1 4.18536
hwhm2 5.27073

```
==> guess SplitGaussian
New function %_1 was created.
==> guess SplitGaussian
New function %_2 was created.
==> guess SplitGaussian
New function %_3 was created.
==> fit
Fit 12 (of 12) parameters to 863 points ...
```

Figure E1 Curve fitting of TS-1(1).

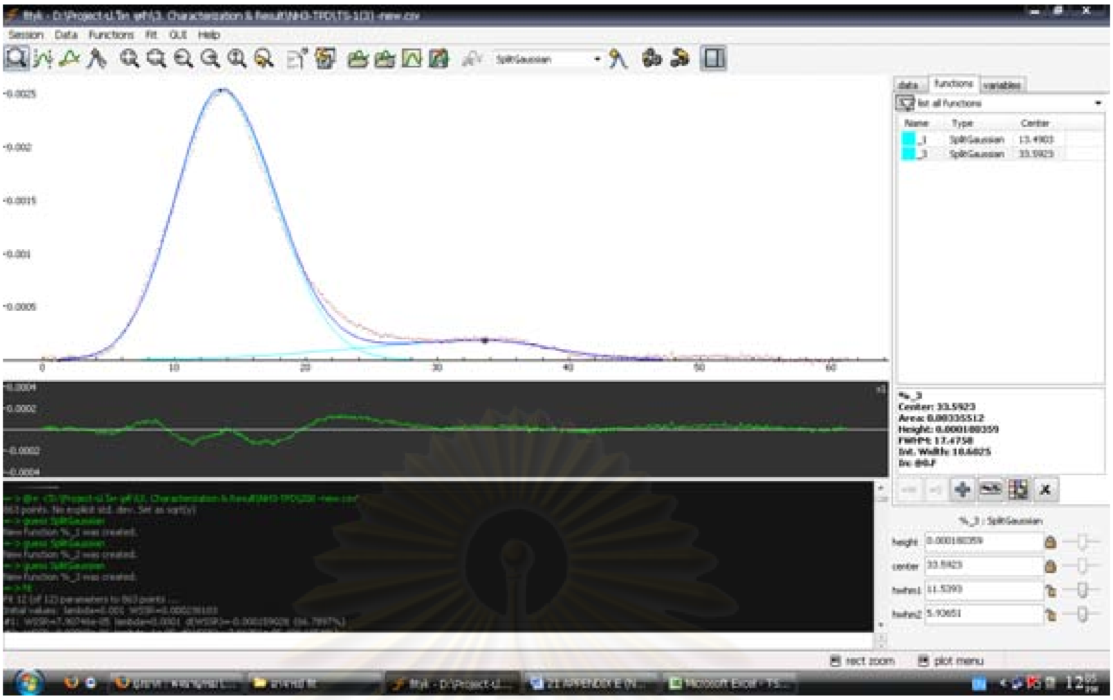


Figure E2 Curve fitting of TS-1(3).

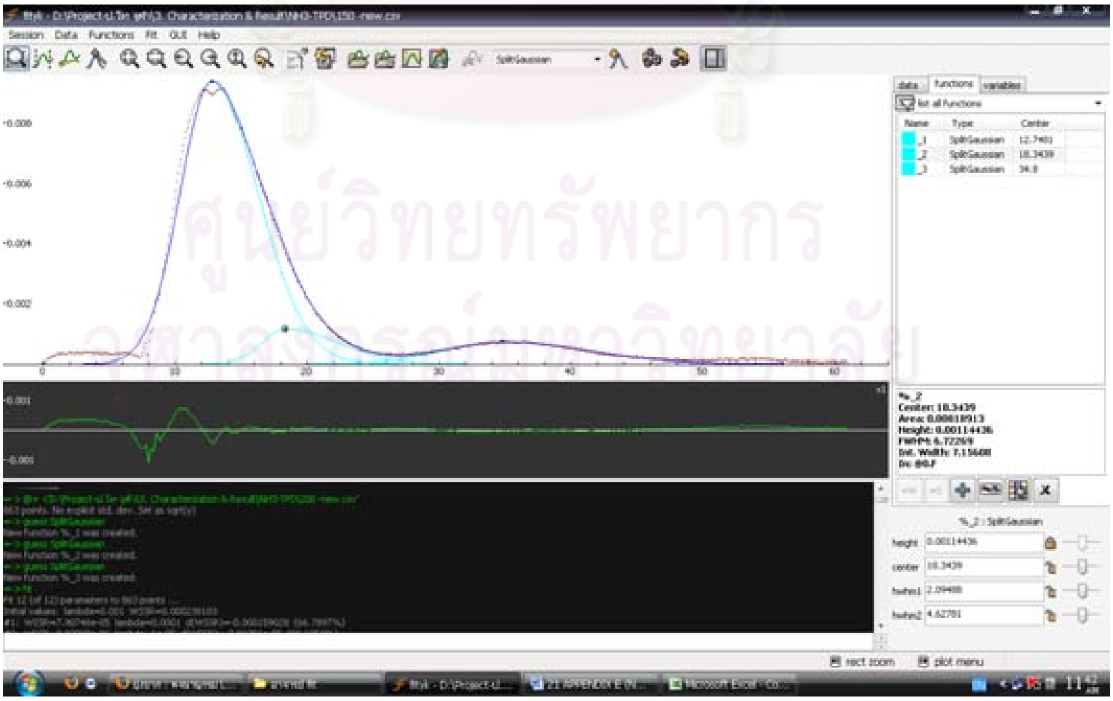
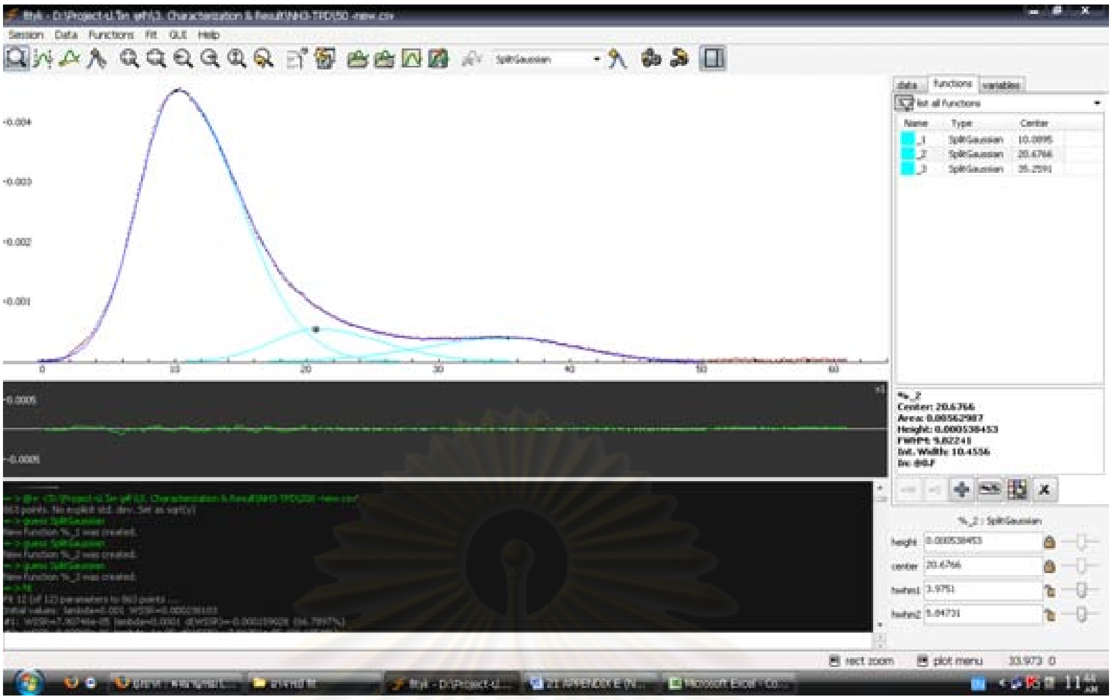


Figure E3 Curve fitting of Co-TS-1(955).

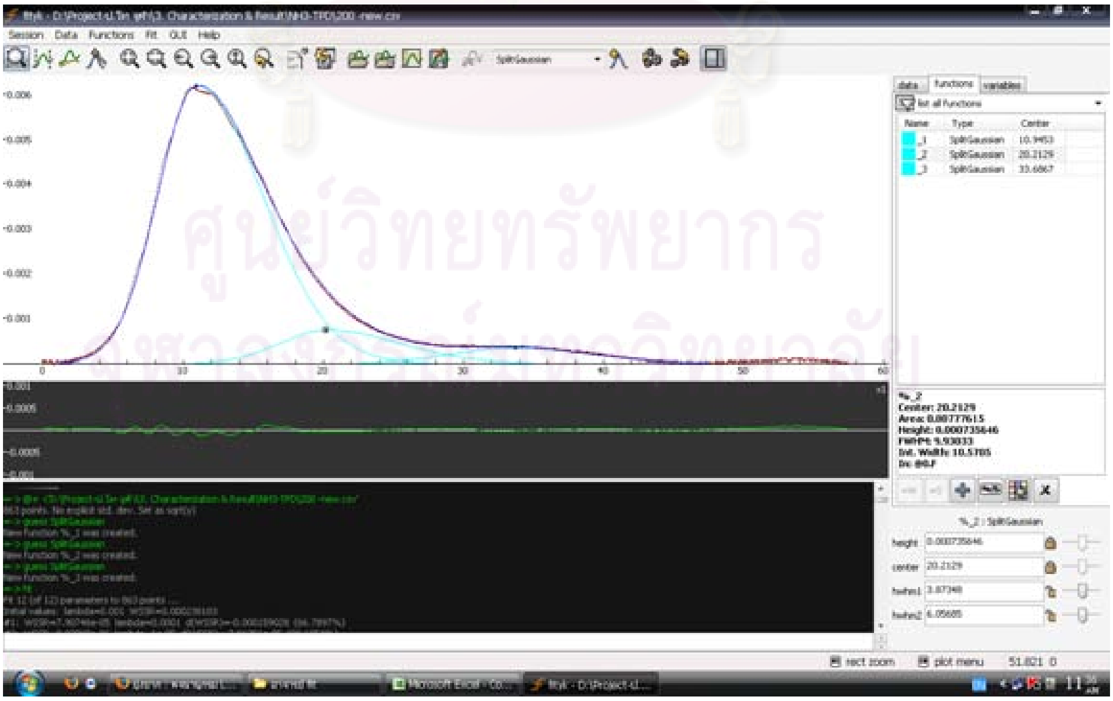


Name	Type	Center
%_1	SplitGaussian	10.0895
%_2	SplitGaussian	20.6766
%_3	SplitGaussian	35.2591

%_2
Center: 20.6766
Area: 0.00562987
Height: 0.000538453
FWHM: 9.82241
Int. Width: 10.4556
Dx: @0.F

%_2 : SplitGaussian
height 0.000538453
center 20.6766
hwhm1 3.9751
hwhm2 5.84731

Figure E4 Curve fitting of Co-TS-1(791).



Name	Type	Center
%_1	SplitGaussian	10.9453
%_2	SplitGaussian	20.2129
%_3	SplitGaussian	33.6867

%_2
Center: 20.2129
Area: 0.00777615
Height: 0.000735646
FWHM: 9.93033
Int. Width: 10.5705
Dx: @0.F

%_2 : SplitGaussian
height 0.000735646
center 20.2129
hwhm1 3.87348
hwhm2 6.05685

Figure E5 Curve fitting of Co-TS-1(591).

APPENDIX F

CALCULATION OF METAL QUANTITY

Example of the calculation of the metal quantity in catalyst

The XRF results were reported in the amount of metal oxide as shown in table F1

Table F1 Data of TS-1(1) from XRF technique

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

Molecular weights of the metal oxides are shown as follow:

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

1. Mole of metal oxides

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

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

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

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

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

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

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

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

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

Table F2 Calculated weight of TS-1(1)

TS-1(1)			**mole of metal oxide**	**mole of cation**	**mole % of cation**	**Mol %**
Compound	**% wt**	**MW**				
Al_2O_3	0.058	101.9613	5.69E-04	0.001707	0.000258	0.025844
SiO_2	97.203	60.0843	1.617777	6.471108	0.98	98.00002
CaO	0.03	56.0774	5.35E-04	0.00107	0.000162	0.016204
TiO_2	2.566	79.8658	3.21E-02	0.128516	0.019463	1.946271
Fe_2O_3	0.041	159.6922	2.57E-04	0.00077	0.000117	0.011665

Table F3 Calculated weight of TS-1(3)

TS-1(3)			**mole of metal oxide**	**mole of cation**	**mole % of cation**	**Mol %**
Compound	**% wt**	**MW**				
Al_2O_3	0.072	101.9613	7.06E-04	0.002118	0.000323	0.032269
SiO_2	95.99	60.0843	1.597589	6.390355	0.97341	97.34101
CaO	0.0199	56.0774	3.55E-04	0.00071	0.000108	0.010811
TiO_2	3.418	79.8658	4.28E-02	0.171187	0.026076	2.607607
Fe_2O_3	0.029	159.6922	1.82E-04	0.000545	0.000083	0.008299

Table F4 Calculated weight of Co-TS-1(955)

Co-TS-1(150)			mole of metal oxide	mole of cation	mole % of cation	Mol %
Compound	**% wt**	**MW**				
Al_2O_3	0.041	101.9613	4.02E-04	1.21E-03	0.00018	0.018365
SiO_2	96.07	60.0843	1.598920	6.395681	0.97366	97.36552
SO_3	0.321	80.0622	4.01E-03	-	-	-
TiO_2	3.285	79.8658	4.11E-02	1.65E-01	0.02505	2.504684
Fe_2O_3	0.033	159.6922	2.07E-04	6.20E-04	0.00009	0.009438
CoO	0.251	74.9326	3.35E-03	6.70E-03	0.00102	0.101989

Table F5 Calculated weight of Co-TS-1(791)

Co-TS-1(50)			mole of metal oxide	mole of cation	mole % of cation	Mol %
Compound	**% wt**	**MW**				
Al_2O_3	0.098	101.9613	9.61E-04	2.88E-03	0.00044	0.043929
SiO_2	96.696	60.0843	1.609339	6.437356	0.98072	98.0722
SO_3	0.56	80.0622	6.99E-03	-	-	-
TiO_2	2.286	79.8658	2.86E-02	1.14E-01	0.01744	1.74427
Fe_2O_3	0.053	159.6922	3.32E-04	9.96E-04	0.00015	0.015169
CoO	0.306	74.9326	4.08E-03	8.17E-03	0.00124	0.124428

Table F6 Calculated weight of Co-TS-1(591)

Co-TS-1(200)			mole of metal oxide	mole of cation	mole % of cation	Mol %
Compound	**% wt**	**MW**				
Al_2O_3	0.07	101.9613	6.87E-04	2.06E-03	0.00031	0.031349
SiO_2	96.215	60.0843	1.601333	6.405334	0.97496	97.49626
SO_3	0.261	80.0622	3.26E-03	-	-	-
TiO_2	3.013	79.8658	3.77E-02	1.51E-01	0.02297	2.296913
Fe_2O_3	0.034	159.6922	2.13E-04	6.39E-04	0.00010	0.009722
CoO	0.408	74.9326	5.44E-03	1.09E-02	0.00166	0.165755

APPENDIX G

FT-IR

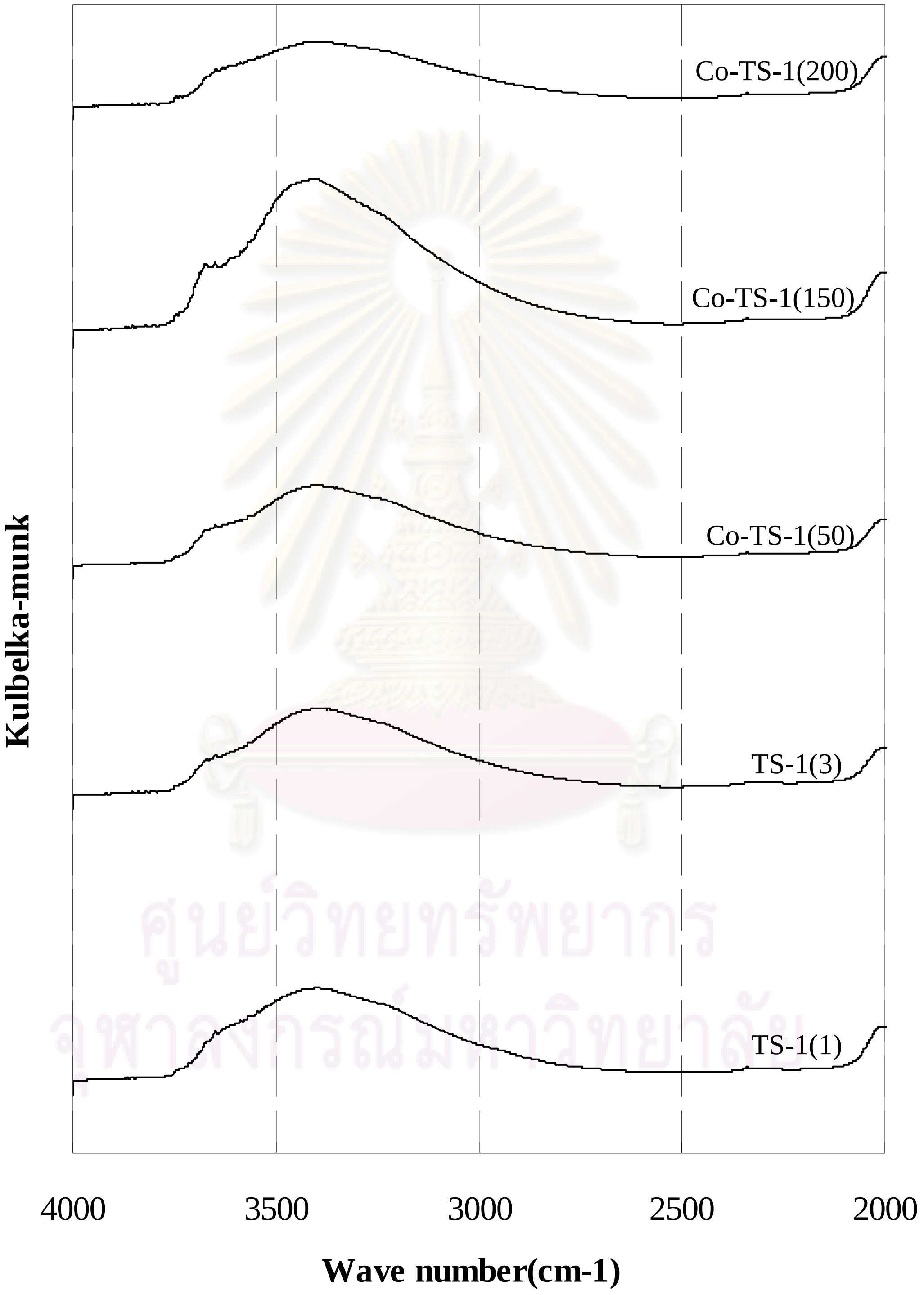


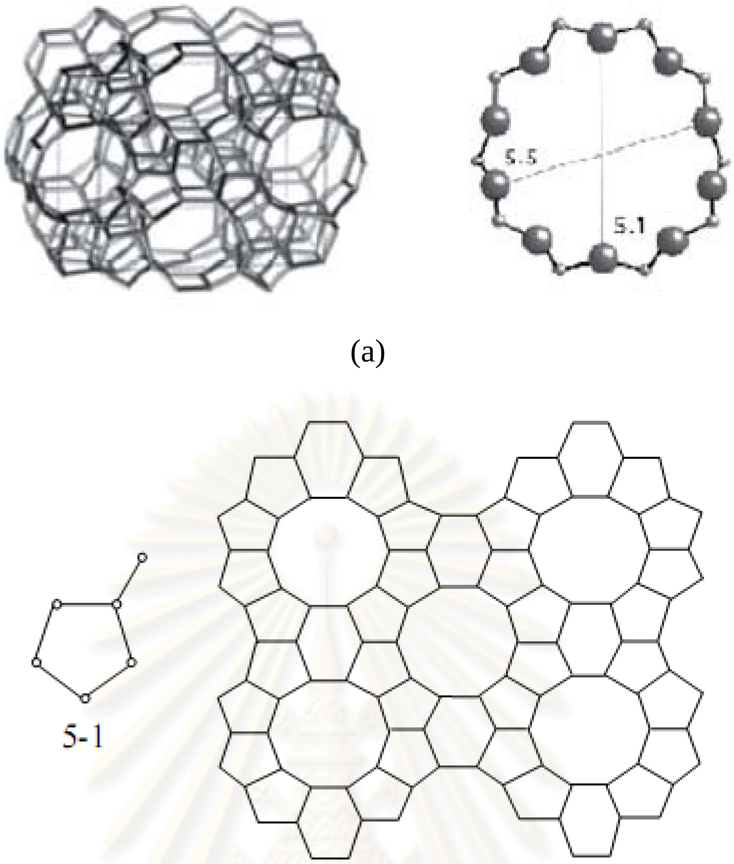
Figure G1 The absorption band of TS-1 and Co-TS-1 in wave number range between 2000 – 4000 cm^{-1}

Appendix H

Titanium silicalite-1

Zeolites are hydratedaluminosilicate that are built from an infinite extending three dimension of AlO_4 and SiO_4 tetrahedra linked to each other by the sharing of oxygen atom. Each AlO_4 tetrahedron in the framework bears a net negative charge which is balanced by a cation, normally from group IA or IIA. The framework contains channels and interconnected voids which are occupied by the cation and water molecules. The cations are movable and may usually be exchanged by other cations.

The topology of the zeolite framework is given by a unique three-letter code which is not related to the composition of the material. ZSM-5 and silicalite-1 are material with MFI topology. As previously mention, the cation may be exchanged and if Si^{4+} exchange with Ti^{4+} these zeolite is called “Titanium silicalite-1”. The MFI structure is a common pattern of crystalline zeolite that is built up by 5-1 secondary building unit (SBU: the smallest number of TiO_4 units, where T is Si or Al but in case of TS-1 at T position is replacing with Si or Ti, from which zeolite topology is built) which are link together to form chain and the interconnection of these chains leads to the formation of the channel system in the structure. The MFI structure has a three dimensional pore system consisting of sinusoidal 10-ring channels (5.1 x 5.5 Å) and intersecting straight 10-ring channels (5.3 x 5.6 Å) (Tosheva et al., 1999). The MFI structure shows in **Figure H1.**



(a)

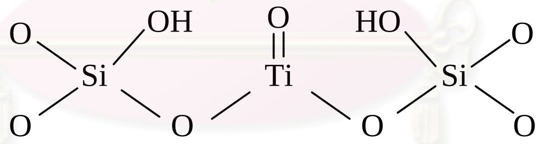
(b)

Figure H1 MFI structure in three dimensional (a) and a 5-1 secondary building unit (b)

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.

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 which is obtained upon silylation.

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.

APPENDIX I

MATERIAL SAFETY DATA SHEET

Toluene

Safety data for toluene

General

Synonyms: methylbenzene, phenylmethane, toluol, antisal 1A, CP 25, methacide, methylbenzol

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, moisture. Highly flammable. Hygroscopic.

Toxicology

Toxic by inhalation, ingestion or by absorption through skin. Serious irritant. Experimental teratogen.

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.

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. Typical OEL 1 ppm.

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 °C

Density (g cm^{-3}): 1.04

Flash point: 63 °C (closed cup)

Explosion limits: 2.1 - 13.5 %

Autoignition temperature: 192 °C

Water solubility: slight

Stability

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

Toxicology

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

Transport information

-

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 ºC
Boiling point: 191 ºC
Vapour density: 3.72
Vapour pressure: 0.3 mm Hg at 20 ºC
Specific gravity: 1.048
Flash point: 81 ºC
Explosion limits:
Autoignition temperature: 598 ºC

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

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: $CH_3C_6H_4OH$

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. Typical TLV/TWA 5 ppm. Typical PEL 5 ppm.

Personal protection

Safety glasses, gloves, adequate ventilation.

APPENDIX J

LIST OF PUBLICATION

Rojarek Passasadee and Tharathorn Mongkhonsi, “Production of cresol from toluene in a one-step reaction”, 18th Thailand Chemical Engineering and Applied Chemistry Conference, Chonburi, Thailand, October, 2008, Ref. No.R030-KC-004-02 (oral presentation).

ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ ม.มหิดล
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Kinetics and Catalysts(cont.)

Production of cresol from toluene in an one step reaction

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Cresol is an organic compound which is widely used in several manufacture processes such as synthesis resins, to dissolve other chemical or used as insecticides. Cresol solutions are used as household cleaners and disinfectants. 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 (2) the methanol alkylation of phenol process to produce cresol. Therefore, the present work introduce a new route to produce cresol in an one step reaction via the hydroxylation of toluene (which is always co-produced with benzene from the reforming process). The present route uses H_2O_2 as the oxidant and titanium silicalite-1 (TS-1) as the catalyst. In addition TS-1 is further modified by adding Co to improve the catalytic selectivity of the catalyst. The catalysts (modified and unmodified) are prepared using different procedures i.e. conventional hydrothermal method (stirring during crystal formation) and static hydrothermal (no stirring during crystal formation). The samples were characterized by XRD, BET, FT-IR and catalytically tested using a three-phase slurry reactor (three neck bottom, 250 ml used as the reactor). XRD shows that all samples have the typical MFI structure. The surface areas are in the range of 324-344 m^2/g. FT-IR shows the absorption band of Ti^{4+} at 960 cm^{-1} in the MFI structure. The hydroxylation of toluene at 70°C shows that TS-1 prepared from the static hydrothermal with 1 day aging yields the highest selectivity of cresols (48.50% p-cresol and 8.60% o-cresol). While the catalyst prepared from the static hydrothermal with 3 day aging shows the highest conversion but leads to the formation of benzaldehyde.

Keywords: titanium silicalite-1 (TS-1), hydrothermal, modified TS-1, hydroxylation of toluene, cresol

Production of cresol from toluene in an one step reaction

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Abstract Cresol can be produced by hydroxylation of toluene with hydrogen peroxide as an oxidant and titanium silicalite-1 (TS-1) as the catalyst. The samples (modified by adding Co and unmodified TS-1 catalysts) are prepared using hydrothermal method. The catalyst samples were characterized by XRD, BET, FT-IR and catalytically tested using the hydroxylation reaction in the slurry reactor. Addition of Co to the TS-1 improves the cresol selectivity of the catalyst. The finding indicates that the prepared catalysts have typical MFI structure and does not appear TiO_2 in the anatase phase. FT-IR shows the absorption band at 960 cm^{-1} which indicates the existence Ti^{4+} in the MFI structure. The hydroxylation of toluene at 70°C shows that Co-TS-1 with atomic ratio of Si/Co equals to 150 has highest conversion of toluene and selectivity toward cresol.

1. Introduction

Cresol is an organic compound which is widely used in several manufacture processes such as synthesis of resins, to dissolve other chemical or used as insecticides. Cresol solutions are used as household cleaners and disinfectants. Cresols (ortho, meta and para isomers) were originally obtained only from coal tar, and after World War II, they were also obtained from spent refinery caustic. Since the mid-1960s, cresols have been produced synthetically on an increasingly large scale so called “Synthetic cresol”**[1]**. 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 i.e. it consists of two steps : (1) the conversion of benzene to phenol via the cumene process (2) the methanol alkylation of phenol process to produce cresol. Therefore, a shorter synthesis routes is still needed.

Titanium silicalite-1 (TS-1) with the MFI structure has been noted as one of the very effective catalyst and attracted much attention because of its unique catalytic properties for the selective oxidation at low temperature such as aromatic hydroxylation **[2]**, propylene epoxidation **[3]**, and styrene oxidation **[4]**. Although, TS-1 has unique catalytic properties at low temperature but it's still has low activity. Many researches have studied several methods to improve the catalytic activity and selectivity of this catalyst. For example, Pirutko et al.**[5]** had added second metals (Al, V, Cr, Fe, Co and Ru) to modified the catalytic activity of TS-1. They found that Fe-TS-1 could catalyze the oxidation of benzene to phenol with high activity and selectivity. Eakawut **[6]** has synthesized modified TS-1 by adding Cu, Co, Cr and V during the synthesis step. The results indicated that the second metal ions and titanium ion could simultaneously and homogeneously incorporated into the framework of TS-1. Pornapa **[7]** has study the catalytic performances of TS-1 and TS-1 modified with second metals (Al, Co, V and Fe) in the hydroxylation toluene and ethyl benzene in a slurry reactor. The results showed that all prepared catalysts could produced cresol(s) but the one modified with Co has the maximum selectivity of cresol.

The main objective of the present work is an extension of a previous study **[7].** The present work studies the potential to produce cresol in an one step reaction via the hydroxylation of toluene with TS-1 and TS-1 modified by adding. All catalyst samples used in the present work were prepared by a static hydrothermal method. The reaction is carried out using a stirred slurry reactor under a triphase condition.

2. Experimental

2.1 Catalyst preparation

The sources of cations are $Co(NO_3)_2.6H_2O$ for Co, $Ti[O(CH_2)_3CH_3]_4$ for Ti, and sodium silicate for Si. TPABr (Tetra-n-propyl ammonium bromide $[(CH_3CH_2CH_2)_4N]Br$) is used as the organic template. The atomic ratio, in the preparation recipe, of Si/Ti is set at 50 and Si/Co is set at 50 and 150, respectively. The detail of the recipes are listed in table 1.

In this study, TS-1 with 1 and 3 days hydrothermal aging are named TS-1(1) and TS-1(3) respectively. The TS-1 modified by adding different amount of Co with 3 days aging are named Co-TS-1(150) and Co-TS-1(50) respectively.

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Table 1 Reagents used for the preparation of TS-1 and Co-TS-1.

Solution for the gel preparation	Solution for decant-solution preparation
Solution A1 $Ti[O(CH_2)_3CH_3]_4$ 2.2085 g TPABr 5.72 g NaCl 11.95 g $Co(NO_3)_2.6H_2O$ x g De-ionized water 60 ml H_2SO_4 (conc.) 3.4 ml	**Solution A2** $Ti[O(CH_2)_3CH_3]$ 2.2085 g TPABr 7.53 g De-ionized water 60 ml $Co(NO_3)_2.6H_2O$ x g H_2SO_4 (conc.) 3.4 ml
Solution B1 Sodium silicate 69 g De-ionized water 45 ml	**Solution B2** Sodium silicate 69 g De-ionized water 45 ml
Solution C1 TPABr 2.16 g NaCl 40.59 g NaOH 2.39 g De-ionized water 208 ml H2SO4 (conc.) 1.55 ml	**Solution C2** NaCl 26.27 g De-ionized water 104 ml

Firstly, a gel mixture is prepared by adding solution A-1 and solution B-1 into solution C-1 drop-wise with vigorous stirring using a magnetic stirrer at room temperature. The pH of the gel mixture is maintained within the range 9-11. The gel mixture is separated from the supernatant liquid by a centrifuge. Secondly, a decantation solution is prepared by adding solution A-2 and solution B-2 into solution C-2, same as for the preparation of gel mixture.

The colourless liquids from A-2, B-2 and C-2 are separated from the mixture by a centrifuge then mixed together again with the milled gel mixture and filled into a pyrex glass which 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°C and kept at this temperature for 1 or 3 days, followed by cooling the mixture to room temperature in the autoclave. The obtained product crystals are washed with de-ionized water by a centrifuge. Then the crystals are dried in an oven at 110°C following by calcination in an air stream at 550°C for 7 h. Before using the catalyst, each catalyst is immersed in a nitric acid solution (5 M) at 80°C for 3 h. After that, the catalyst is washed with distilled water until pH 7, dried at 110°C and calcined again at 540°C for 7 h in static air.

2.2 Catalyst characterization

The crystallinity of the catalysts was identified by a X-ray diffractometer SIEMENS D5000 connected with a computer with Diffract AT version 3.3 programme for fully control of the XRD analyzer. The measurements were carried out by using Cu Kα radiation. Measurements were performed over the 2 theta ranges from 6 to 30 degree with step size 0.04 °/sec.

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

The chemical composition analysis of elements of the catalyst is performed by X-ray fluorescence (XRF) using Oxford model ED2000.

The surface area is measured using the BET technique using Micromeritrics ASAP 2020. The sample cell which contained 0.1 g of sample was used for each measurement.

2.3 Catalytic Performance

The hydroxylation of toluene with H_2O_2 (30 wt% in water, Merk) is carried out in a 250 ml, water jacketed, there-necked, glass flask fitted with a condenser and a magnetic stirrer placed in a stirring an oil bath. The reaction is performed at atmospheric pressure. Typically, 1 g of the catalyst is reacted with reactants i.e. toluene to H_2O_2 molar ratio equals to 1 to 1 and 50 ml of water. In the beginning, the catalyst and water, using for dispersion of the catalyst, are added into the reactor at 90°C for 1 h to drive out gases in pores of the catalyst. Then the reactor is cooled down to 70°C and 1 ml of toluene is added into the reactor. H_2O_2 is slowly injected drop-wise by using a 1 ml syringe at 70ºC for 2 h. After that the reaction is terminated by rapid cooling and 50 ml of ethanol is added into reactor to homogenize the aqueous phase and the organic phase. The products are analyzed by a gas chromatograph equipped with a FID detector (SHIMADZU GC9A).

3. Result and discussion

3.1 Characterization of catalysts

3.1.1 X-ray diffraction (XRD)

The XRD spectra of TS-1 and modified with Co (Co-TS-1) are shown in Figure 1. All spectra consist of six main characteristic peaks at 2 theta ≈ 8°, 8.8°, 14.8°, 23.1°, 24° and 26.7°**[8]** that indicate the typical MFI pattern and high crytalinity. The absence of the pattern of anatase 2 theta ≈ 25.3° confirms that anatase does not exist in the prepared catalsyts. The single peaks at 2 theta ≈ 24.4 and 26° indicate an orthorhombic symmetry typical of TS-1 with a framework Si/Ti < 100 **[9]**.

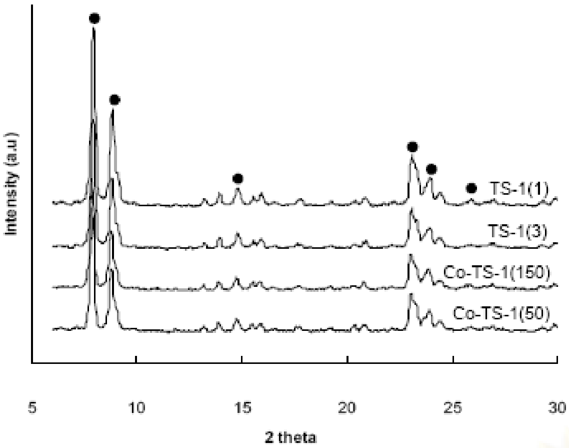

Figure 1 XRD pattern of TS-1 and modified TS-1.

3.1.2 Fourier-transform Infrared spectroscope (FT-IR)

FT-IR is a useful tool to characterize framework titanium. The catalytic performance of TS-1 is related to the amount of Ti in the framework **[9]**. FT-IR spectra of all samples are shown in Figure 2. The characteristic absorption band of tetrahedral Ti^{4+} in the TS-1 and Co-TS-1 appears at about 960 cm^{-1}, which indicates that titanium has been incoporated into the framework **[2,10]**.

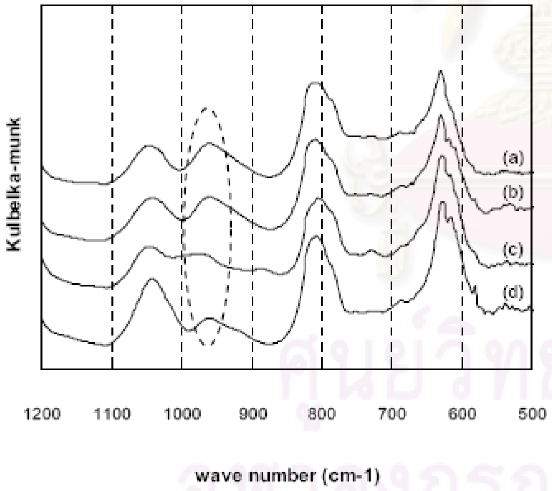

Figure 2 IR spectra of TS-1 and modified TS-1 : TS-1(1) (a), TS-1(3) (b), Co-TS-1(150) (c) and Co-TS-1(50) (d).

3.1.3 Determination of composition by X-ray Fluorescence spectroscopy (XRF).

The compositions of TS-1 and modified TS-1 are shown in Table 3 below. It should be noted here that though the same amount of Ti was used for each catalyst, the amount of Ti atoms can be incorporated in the TS-1 structure are not the same. This suggests that the presence of another metal species affects the ability of Ti^{4+} ion in the formation of TS-1 structure. The mechanism why the second metal ion affects the incorporation of Ti^{4+} has yet to be a subject of further studied.

Table 2 XRF analysis TS-1 and Co-TS-1

Samples	%Si	%Ti	%Co	%Si/Ti	%Si/Co
TS-1(1)	97.20	2.57	none	37.88	none
TS-1(3)	95.90	3.42	none	28.06	none
Co-TS-1(150)	93.35	4.19	1.32	22.27	70.72
Co-TS-1(50)	94.05	3.99	1.58	23.57	59.53

3.1.4 Determination of surface area by BET

The surface areas of all catalysts investigated that the surface areas of TS-1 and Co-TS-1 are in range of 320-340 m²/g.

3.2 The catalytic reaction of hydroxylation of toluene

The results of the hydroxylation of toluene using TS-1 and modified TS-1 with Co (Co-TS-1) at 70°C for 2 h are shown in Figure 3. All samples give the same reaction products : benzaldehyde, o- cresol and p- cresol. The catalytic activity is in the following order Co-TS-1(150) > TS-1(1) > Co-TS-1(50) > TS-1(3). The maximum conversion was achieved with Co-TS-1(150) about 0.908. The absence of m-cresol is due to the fact that the methyl group ($-CH_3$) is an ortho- and para-directing group for the electrophilic substitution of the benzene ring.

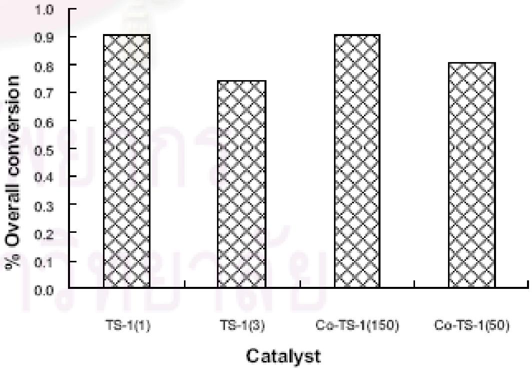

Figure 3 The hydroxylation of toluene at 70°C.

The selectivity of each catalyst is shown in Figure 4. In case of unmodified TS-1, TS-1(1) has higher selectivity of o-cresol and p-cresol than TS-1(3). But after adding Co to TS-1(3), the formation of benzaldehyde is suppressed and the selectivity towards cresols increases. In addition, it is found that Co-TS-1(150) performs better selectivity towards cresols than Co-TS-1(50).

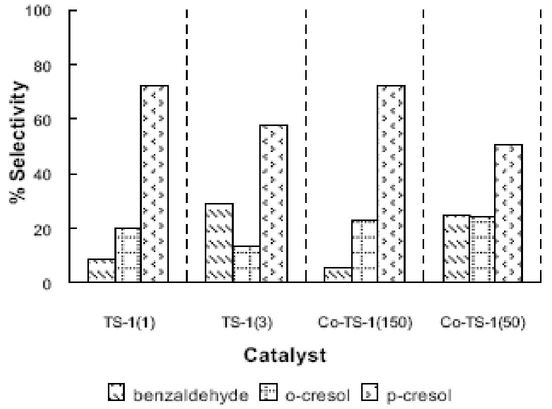

Figure 4. The selectivity of hydroxylation of toluene at 70°C

The productivity of all catalysts is shown in Figure 4. The figure clearly shows that, among the catalysts investigated, Co-TS-1(150) exhibits the best catalytic activity and selectivity towards both of *o*- and *p*-cresol.

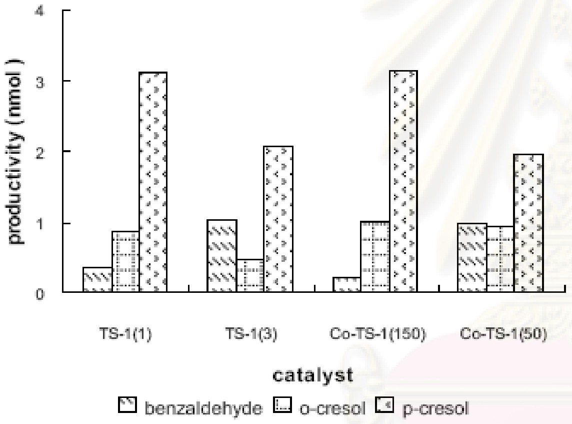

Figure 5 The productivity of TS-1 and Co-TS-1

4. Conclusion

The present work found that o- and p-cresol can be produced in a single step reaction, the hydroxylation of toluene by H_2O_2 using TS-1 and TS-1 modified by adding Co. All catalysts investigated in the present study have MFI structure and does not appear Ti in anatase phase. The hydroxylation of toluene produced *o*-cresol, *p*-cresol and benzaldehyde. The modification of TS-1 with an appropriate amount of Co can improved catalytic activity and selectivity. The catalytic activity observed in the present study is in the following order Co-TS-1(150) > Co-TS-1(50) > TS-1(1) > TS-1(3).

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