การศึกษาคุณสมบัติการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาไทเทเนียม ซิลิกาไลต์-1 ปรับปรุงโดยโคบอลต์ในปฏิกิริยาไฮดรอกซิเลชันของโทลูอีนโดยใช้ไฮโดรเจนเปอร์ออกไซด์

นางสาว ศิยา อุดมชัชวาล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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ปีการศึกษา 2551

CATALYTIC STUDY OF COBALT MODIFIED TITANIUM SILICALITES-1 IN THE HYDROXYLATION OF TOLUENE TO CRESOL BY HYDROGEN PEROXIDE

Miss Siya Udomchatchawan

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
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Thesis Title	CATALYTIC STUDY OF COBALT MODIFIED TITANIUM SILICALITES-1 IN THE HYDROXYLATION OF TOLUENE TO CRESOL BY HYDROGEN PEROXIDE
By	Miss Siya Udomchatchawa
Field of Study	Chemical Engineering
Thesis Advisor	Associate Professor Tharathon Mongkhonsi, Ph.D.

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

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ศิยา อุดมชัชวาล: การศึกษาคุณสมบัติการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาไทเทเนียม ซิลิกาไลต์-1 ปรับปรุงโดยโคบอลต์ในปฏิกิริยาไฮดรอกซิเลชันของโทลูอีนโดยใช้ไฮโดรเจนเปอร์ออกไซด์ (CATALYTIC STUDY OF COBALT MODIFIED TITANIUM SILICALITES-1 IN THE HYDROXYLATION OF TOLUENE TO CRESOL BY HYDROGEN PEROXIDE) อ. ที่ปรึกษาวิทยานิพนธ์หลัก :รศ.ดร.ธราธร มงคลศรี, 123 หน้า

งานวิจัยนี้ได้ศึกษาปฏิกิริยาไฮดรอกซิเลชันของโทลูอีนด้วยไฮโดรเจนเปอร์ออกไซด์ในเครื่องปฏิกรณ์แบบฟองแก๊สโดยใช้ตัวเร่งปฏิกิริยาไทเทเนียมซิลิกาไลต์-1ที่ถูกปรับปรุงด้วยโลหะโคบอลต์ (Co-TS-1) การเกิดปฏิกิริยากระทำที่อุณหภูมิ 70 องศาเซลเซียสและความดันบรรยากาศ ปัจจัยที่ศึกษาได้แก่ความเข้มข้นของไฮโดรเจนเปอร์ออกไซด์ปริมาณที่เหมาะสมของโลหะโคบอลต์ เวลาที่ใช้ในการตกผลึก และผลของการปรับสภาพตัวเร่งปฏิกิริยาด้วยการล้างด้วยกรดไนตริก ผลการทดลองแสดงให้เห็นว่าการเติมเกลือโคบอลต์ในปริมาณที่มากเกินไปก่อนการตกผลึกตัวเร่งปฏิกิริยาจะทำให้ไอออนโคบอล์ตไม่เข้าไปอยู่ในโครงสร้างผลึกแต่จะรวมตัวกันเป็นสารประกอบโคบอลต์ที่ถูกชะล้างออกด้วยสารละลายกรดไนตริกได้การชะล้างสารประกอบโคบอลต์ดังกล่าวออกไปยังช่วยให้ความว่องไวของตัวเร่งปฏิกิริยาสูงขึ้นด้วยผลการทำปฏิกิริยาแสดงให้เห็นว่าครีซอลจะเกิดได้ดีที่ความเข้มข้นไฮโดรเจนเปอร์ออกไซด์ต่ำที่ความเข้มข้นไฮโดรเจนเปอร์ออกไซด์ร้อยละ 3 จะได้ค่าการเลือกเกิดครีซอลถึงร้อยละ 100 ที่ความเข้มข้นไฮโดรเจนเปอร์ออกไซด์สูงมากเกินไปจะทำให้ได้เบนซาลดีไฮด์เป็นผลิตภัณฑ์หลักแทน

ภาควิชา..............วิศวกรรมเคมี.......... ลายมือชื่อนิสิต.........ศิยา.........................
สาขาวิชา............วิศวกรรมเคมี.......... ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก.....................
ปีการศึกษา..........2551.....................

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KEY WORD: TS-1/CO-TS-1/ MODIFIED TS-1/TOLUENE/BUBBLE REACTOR/ HYDROXYLATION

SIYA UDOMCHATCHAWAN: CATALYTIC STUDY OF COBALT MODIFIED TITANIUM SILICALITES-1 IN THE HYDROXYLATION OF TOLUENE TO CRESOL BY HYDROGEN PEROXIDE:
ADVISOR: ASSOC.PROF. THARATHON MONGKHONSI, Ph.D., 123 pp.

This research investigated the hydroxylation of toluene by hydrogen peroxide in a bubble reactor using titanium silicalite-1 (TS-1) catalysts modified with Co. The reaction is carried out at 70° C and atmospheric pressure. Parameters investigated are hydrogen peroxide concentration, appropriate amount of cobalt, crystallization time, and effects of treatment (washing with nitric acid solution). The experimental results show that the addition of too much cobalt salt before catalyst crystallization results in the separation of cobalt cation from the catalyst crystal structure. Such excess cobalt will form a cobalt compound which can be washed off with nitric acid solution. The washing of such cobalt compound can increase the catalytic activity of the catalyst. Reaction study shows that the formation of cresol prefers a low hydrogen peroxide concentration. At 3wt% hydrogen peroxide concentration, selectivity toward cresol up to 100% can be achieved. At a too high hydrogen peroxide concentration, benzaldehyde becomes the main reactor product.

Department:…Chemical Engineering… Student's Signature……ศิยา……………….
Field of Study:…Chemical Engineering.. Advisor's Signature……………………
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Finally, she would like to dedicate the achievement of this work to her parents (Mr. Siri Udomchatchawan, Ms. Pheeya Udomchatchawan) who have always been the source of her suggestion, support and encouragement.

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CHAPTER I

Introduction

Cresols have a wide variety of uses including the manufacture of synthetic resins, tricresyl phosphate, salicylaldehyde, coumarin, and herbicides. cresol molecule has a methyl group substituted onto the benzene ring of a phenol molecule. There are three forms of cresols that are only slightly different in their chemical structure: ortho-cresol (o-cresol), meta-cresol (m-cresol), and para-cresol (p-cresol). These forms occur separately or as a mixture. An approximate breakdown of cresol and cresylic acid use is 20% phenolic resins, 20% wire enamel solvents, 10% agricultural chemicals, 5% phosphate esters, 5% disinfectants and cleaning compounds, 5% ore flotation, and 25% miscellaneous and exports.

The oldest cresol production method used in the United States is through the recovery of fractional distillates from coal tars. Most domestic cresols are formed via catalytic and thermal cracking of naphtha fractions during petroleum distillation. Since 1965, quantities of coal tar and petroleum have been insufficient to meet the rising demand. Consequently, several processes for the manufacture of the various isomers have been developed. One General Electric facility produces cresol by the methylation of phenol which phenol is produced by three stage of cumene or hydroxylation of benzene. Since in real industrial practice, benzene and toluene are always co-produced (from the catalytic reforming process), this research interests in the direct addition of an –OH group to the ring of toluene. This process should have advantage over the current process that cresol can be produced in only one step

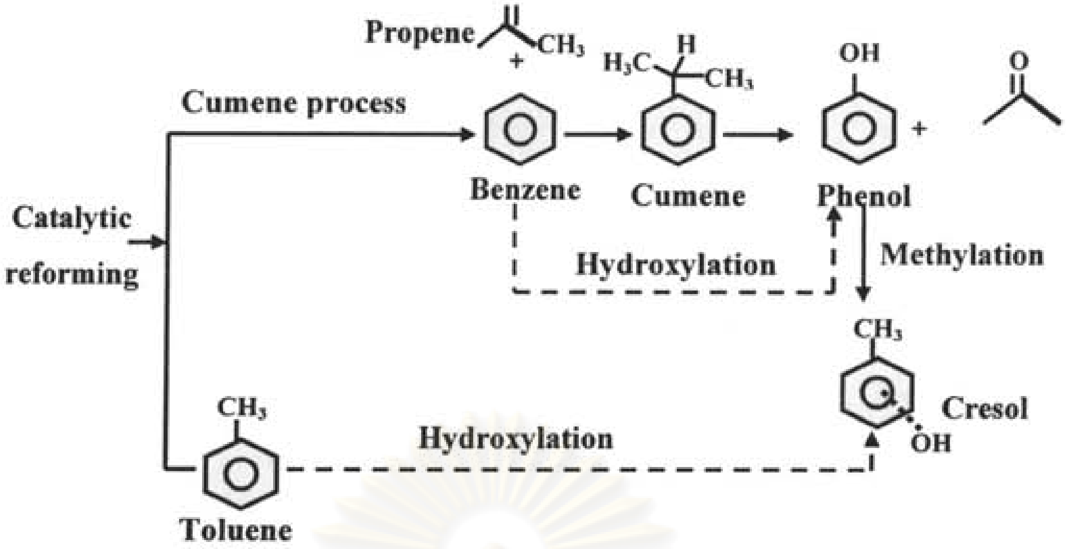


Figure 1 The routes of cresol production from phenol and toluene

Therefore, a new route to produce cresol in one step is demanded and the concept of the hydroxylation of benzene to phenol is a guide line. For the overall diagram of cresol production by using phenol methylation path and a new proposed route are illustrated in Figure 1. Since in industrial, benzene and toluene are always co-produced (from the catalytic reformer), to produce cresol with the direct hydroxylation of toluene by H_2O_2 as oxidant is considered in this research.

The discovery of titanium silicalite-1 (TS-1) which is a zeolite of the pentasil family by Taramasso and co-worker in 1983 opened a new route for the catalysis and catalytic reaction. The new material has attracted a great deal of attention. Structurally, the titanium in TS-1 isomorphously replaces silicon in a tetrahedral site of the MFI silicalite lattice. As such, it combines the advantages of the high coordination ability of Ti^{4+} ions with the hydrophobicity of the silicalite framework, while retains the spatial selectivity and specific local geometry of the active sites of molecular sieve structure.

There are many types of reactor using for hydroxylation such as catalytic membrane reactor (Molinari et al., 2006), fixed bed and recycle reactor (Reitzmann et al., 2002), glass batch reactor (Kumar et al., 1999) and electrochemical cells reactor (Otsuka and Yamanaka, 1998). From a former researcher (Manit, 2006) studied in the bubble reactor which are widely used in chemical industry where heterogeneous gas-liquid or gas-solid reaction take place, particularly, in which the liquid phase controls mass transfer processes due to the relative insolubility of gases. Therefore, the bubble reactor is chosen as reactor in present work.

Pirutko et al. (2001) reported that the metal modified TS-1 catalysts gave a higher phenol conversion rate than TS-1. he found that the metal modified of TS-1 catalysts by adding Co during the synthesis step by a hydrothermal method. It has been reported that loading transition metals to TS-1 up to a level still maintained the MFI structure. In addition, the oxidation properties of metal modified TS-1 and pretreatment of catalysts in the hydroxylation of benzene with H_2O_2 as the oxidizing agent have never been studied before.

Previously, the hydroxylation is performed in liquid phase that the catalyst surface is mostly covered by the adsorbed toluene and left only a small area for H_2O_2 to present on the catalyst surface. The consequence is low reaction rate. An attempt has been made to enhance the adsorption of H_2O_2 by changing toluene feeding method (bubble reactor). In the bubble reactor, the catalyst is firstly dispersed in H_2O_2 in a slurry form to allow H_2O_2 to be the first species that cover the catalyst surface. Then, toluene vapor is bubble through the slurry. Due to the concentration of toluene is reduced and toluene is introduced secondly, the portion of the catalyst surface covered by H_2O_2 is expected to be higher than feeding toluene in liquid phase.

In the present work, the objective is to study oxidation properties of TS-1 and Co-TS-1treatment with HNO_3 solution in the hydroxylation of toluene by hydrogen peroxide as an oxidant in a bubble flow reactor. The research has been scoped as follows:

Scopes of this research

1) Preparation of Co-TS-1 catalysts which have 50 Si to Ti and 50, 150 and 300 ratio by using the incorporation method.

2) Treatment of these catalysts with 5M HNO_3 solution

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

- Determination of bulk composition of Si, Ti and Co by X-ray fluorescence (XRF).
- Determination the surface area and pore volume by N_2 Adsorption based on BET method (BET).
- Determination of structure and crystallinity of catalysts by X-ray diffractrometer (XRD).
- Determination of incorporation of Ti atoms as a framework element by IR Spectroscopy (IR).
- Determination of acid sites of the synthesize catalysts by NH_3-TPD technique.

4) Investigate catalytic behavior of synthesized catalysts are evaluated by three phase hydroxylation toluene using hydrogen peroxide as an oxidant in bubble reactor at 70 °C.

5) Influence of concentration of hydrogen peroxide that affect on synthesized catalysts in hydroxylation of toluene.

This present work is organized as follows:

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

Chapter II collects theory of aromatics substitution and reviews research works on the hydroxylation of toluene on TS-1 catalysts.

Chapter III consists of catalysts preparation, catalysts characterization and catalytic reaction study the hydroxylation of toluene in a bubble reactor.

The characterization of synthesized catalysts and results of hydroxylation of toluene, including an expanded discussion, are described in chapter IV.

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

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

CHAPTER II

THEORY AND LITERATURE REVIEWED

2.1 Titanium silicalite – 1

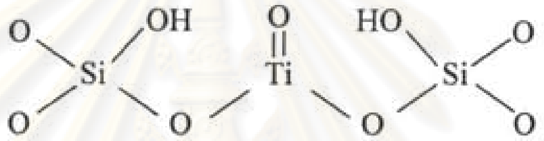
Titanium silicalite is an interesting material obtained by isomorphic substitution of trivalent metals or tetravalent metals in the framework of crystalline aluminosilicates or silicates. Titanium silicalites with MFI (TS-1) and MFI/MEL (TS-2) structures have been used in several oxidation reactions with H_2O_2 as the oxidizing agent.

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 particular, extra-framework massive Ti-oxides, as well as other contaminants, cause undesirable side reactions, and, as a consequence, losses of activity and selectivity of the catalyst.

2.2 Hydrothermal method

Hydrothermal methods utilize water under pressure and at temperatures above its normal boiling point as a means of speeding up the reaction between solids. The water performs two roles. The water as liquid or vapor serves as the pressure transmitting medium. In addition, some or all of the reactants are partially soluble in water under pressure and this enables reactions to take place in, or with the aid of, liquid and/or vapor phases. Under these conditions, reactions may occur that, in the absence of water, would occur only at much higher temperatures. The method is therefore particularly suited for synthesis of phases that are unstable at higher temperatures. It is also a useful technique for growth of single crystals; by arranging for a suitable temperature gradient to be present in the reaction vessel, dissolution of the starting material may occur at the hot end and reprecipitation at the cooler end.

Since hydrothermal reactions must be carried out in closed vessels, the pressure-temperature relations of water at constant volume are important. These are shown in The critical temperature of water is 374 °C. Below 374 °C, two fluid phases, liquid and vapor can coexist. Above 374 °C only one fluid phase, supercritical water, ever exists. Curve AB presents the saturated stream curve. At pressures below this curve liquid water is absent and the vapor phase is not saturated with respect to steam; on the curve the vapor is composed of saturated stream which is in equilibrium with liquid water; above the curve, liquid water is effectively under compression and the vapor phase is absent.

The dashed curves in Figure 2.1 maybe used to calculate the pressure that is developed inside a vessel after it has been partially filled with water, closed and heated to a certain temperature. Thus, curve BC corresponds to a vessel that is initially 30 percent full of water: at, for example, 600 °C, a pressure of 800 bar is generated inside the closed vessel. Although Figure 2.1 applies strictly to pure water, the curves are modified little, provided the solubility of solids present in the reaction vessel is small.

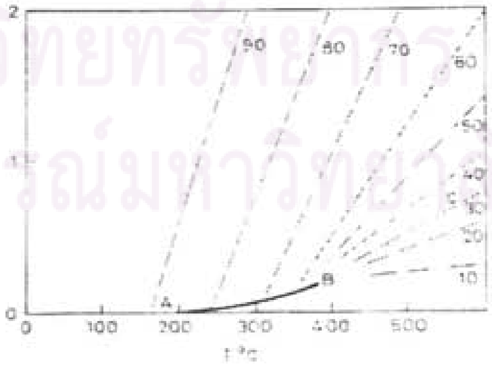


Figure 2.1 Pressure-temperature relations of water at constant volume. Dashed curves represent pressures developed inside a closed vessel; numbers represent percentage degree of filling of the vessel by water at ordinary P, T. (http://ocw.nctu.edu.tw/upload/sschemistry/sschemistry_lecturenotes/ssch-9-1.pdf)

The design of hydrothermal equipment is basically a tube, usually of steel closed at one end. The other end has a screw cap with a gasket of soft copper to provide a seal. Alternately, the bomb may be connected directly to an independent pressure source, such as a hydraulic ram; this is known as the cold seal method. The reaction mixture and an appropriate amount of water are placed inside the bomb which is then sealed and placed inside an oven at the required temperature.

2.3 Hydroxylation of toluene

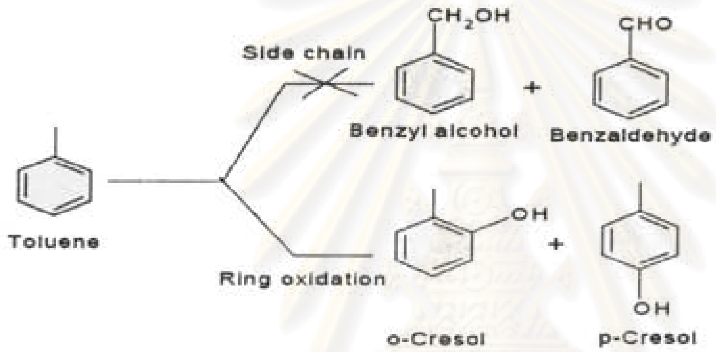


Figure 2.2 Hydroxylation of toluene over titanium silicalite (TS-1) catalyst.

The products and rout of hydroxylation toluene are presented in Figure 2.2, it was obtained o-cresol and p-cresol from the ring oxidation

Effect of time was observed the reaction was fast at beginning. The increment of conversion and H_2O_2 efficiency with time was associated with progressive increasing p-selectivity.

Effect of toluene to H_2O_2 molar ratio was observed increasing this ratio, there was progressive increasing H_2O_2 efficiency as well as para-selectivity. At low ratio, the selectivity for para-cresol was less compared to that at higher molar ratio. The active species inside the pore might be mainly contributing catalytic site.

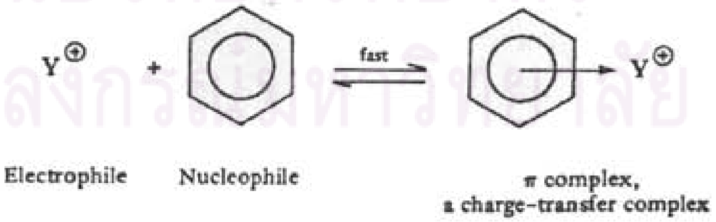
Effect of diluted level was observed the increasing dilution made H_2O_2 efficiency and para-cresol selectivity to increase.

Effects of different Ti content of TS-1 catalyst were studied. The results were observed the increasing Si/Ti ratio, there was a progressive increase in para-cresol, although, there was a decrease in H_2O_2 efficiency. This could be explained with the relatively hydrophobic behavior of different TS-1 species. It would increase with decreasing Ti-content in catalyst. The less the amount of Ti- would be the local polarization of Si-O-Ti bound and more hydrophobicity. The adsorption of the hydrophobic molecules inside the TS-1 channels leaded to the increase shape selective para product.[Mukherjee (2000)]

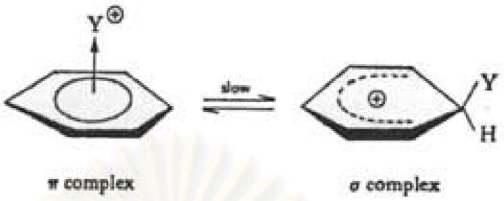
2.4 Electrophilic aromatics substitution

Due to its π-electron cloud the benzene molecule has basis (nucleophilic) properties. Benzene reacts mainly with electrophilic reagents. In these reactions a hydrogen atom of benzene is displaced (substituted) by an electrophilic reagent. This important type of reaction is called "electrophilic aromatic substitution". The electrophilic aromatic substitution involves several steps.

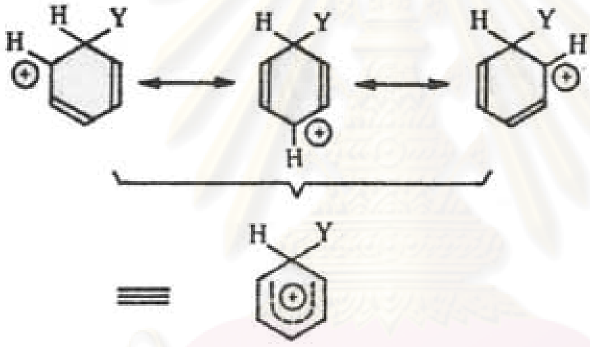
A π complex is formed. The electrophilic reagent $Y^{\oplus}$ is attracted by the nucleophilic π-electron cloud of benzene and is loosely held.

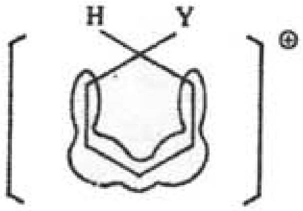


A conjugated carbonium ion is formed. The electrophilic reagent $Y^{\oplus}$ in the π complex attaches to a particular carbon atom, which thereby becomes sp^3-hybridized. The positive charge is delocalized over the other five carbons which are still in the sp^2 state and remain in one plane with the sp^3-hybridized carbon. Thus the orbital of the sp^2-hybridized carbons can overlap and the resonance-stabilized carbonium ion, known as a σ complex, is formed. During this reaction complete delocalization of the π electrons in benzene must be interrupted. This is therefore the slowest and rate-determining step, requiring a high energy of activation.



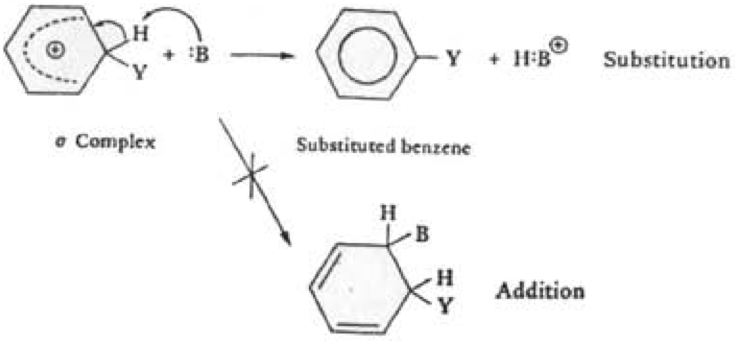
The σ complex is a resonance hybrid of three contributing structures. The positive charge is mainly in *o* or *p* positions.





Electron density in the phenonium ion

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



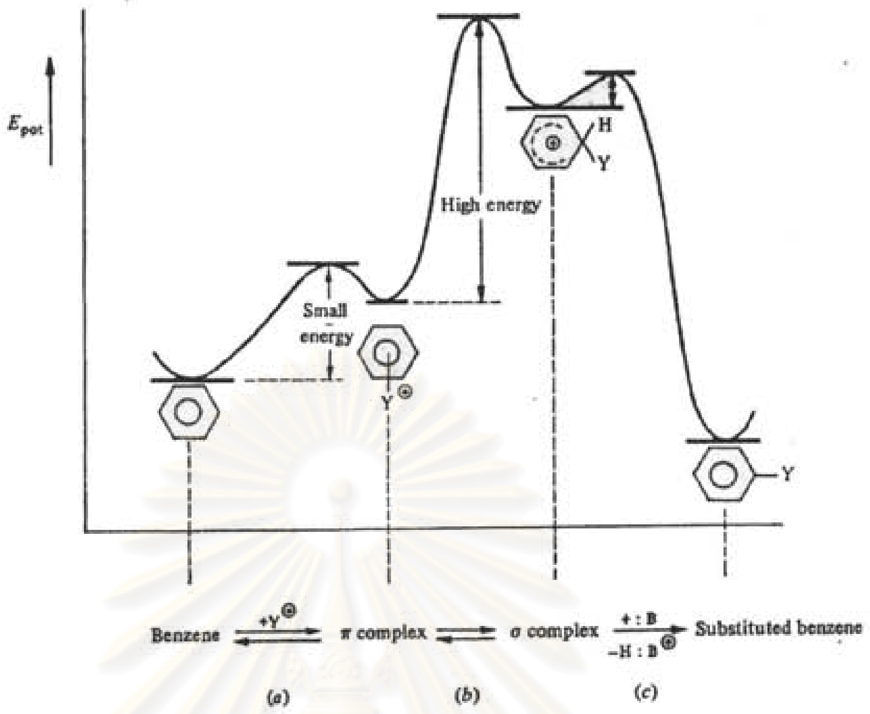


Figure 2.3 Energy profile of electrophilic aromatic substitution on benzene ring. (Zlatkis et al., 1985)

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

2.5 Effects of substitution

When substituted benzene compounds undergo electrophilic substitution reactions of the kind discussed above, two related features must be considered.

1) The first is the relative reactivity of the compound compared with benzene itself. Experiments have shown that substituents on a benzene ring can influence reactivity in a profound manner. For example, a hydroxy or methoxy substituent increases the rate of electrophilic substitution about ten thousand fold. In contrast, a nitro substituent decreases the ring's reactivity by roughly a million. This activation or deactivation of the benzene ring toward electrophilic substitution may be correlated with the electron donating or electron withdrawing influence of the substituents, as

measured by molecular dipole moments. The dipole moment of the symmetrical benzene molecule is zero. Monosubstituted benzenes have unsymmetrical electron density distributions. Electron donating groups increase the electron density of the benzene nucleus making the nucleus more nucleophilic toward electrophilic reagents. These groups activate the aromatic ring system. Electron withdrawing groups decrease the electron density of the benzene nucleus making the nucleus less nucleophilic toward electrophilic reagents. These groups deactivate the aromatic ring system. In Figure 2.2 we see that electron donating substituents (blue dipoles) activate the benzene ring toward electrophilic attack, and electron withdrawing substituents (red dipoles) deactivate the ring (make it less reactive to electrophilic attack).

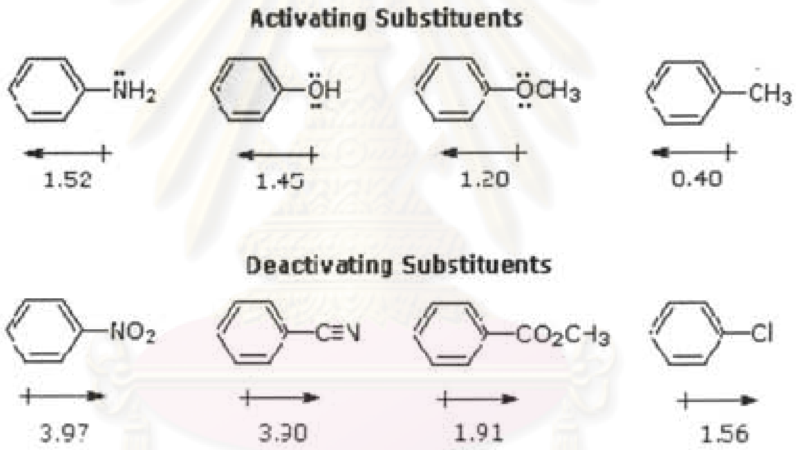


Figure 2.4 Diagram of electron donating substituents (blue dipoles) activate the benzene ring and electron withdrawing substituents (red dipoles) deactivate the ring. (www.cem.msu.edu/~reusch/VirtualText/benzrx1.htm#benz5)

The influence a substituent exerts on the reactivity of a benzene ring may be explained by the interaction of two effects: The first is the inductive effect of the substituent. Most elements other than metals and carbon have a significantly greater electronegativity than hydrogen. Consequently, substituents in which nitrogen, oxygen and halogen atoms form sigma-bonds to the aromatic ring exert an inductive electron withdrawal, which deactivates the ring. The second effect is the result of conjugation of a substituent function with the aromatic ring. This conjugative interaction facilitates electron pair donation or withdrawal, to or from the benzene ring, in a manner different from the inductive shift. If the atom bonded to the ring has one or more non-bonding valence shell electron pairs, as do nitrogen, oxygen and the halogens, electrons may flow into the aromatic ring by p-π conjugation (resonance). Finally, polar double and triple bonds conjugated with the benzene ring may withdraw electrons. In both cases the charge distribution in the benzene ring is greatest at sites ortho and para to the substituent. Sometimes these two effects are opposite to one another. One effect may be stronger and exert greater influence

2) The second factor that becomes important in reactions of substituted benzenes concerns the site at which electrophilic substitution occurs. Since a monosubstituted benzene ring has two equivalent ortho-sites, two equivalent meta-sites and a unique para-site, three possible constitutional isomers may be formed in such a substitution, as shown in Figure 2.3. If reaction occurs equally well at all available sites, the expected statistical mixture of isomeric products would be 40% ortho, 40% meta and 20% para. In addition, the nature of the substituent influences in this product ratio in a dramatic fashion such as bromination of methoxybenzene (anisole) is very fast and gives mainly the para-bromo isomer, accompanied by 10% of the ortho-isomer and only a trace of the meta-isomer. Bromination of nitrobenzene requires strong heating and produces the meta-bromo isomer as the chief product.

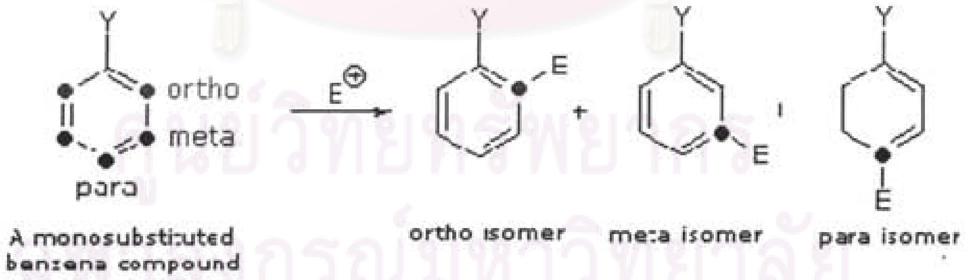


Figure 2.5 The position of monosubstituted electrophile on benzene ring. (www.cem.msu.edu/~reusch/VirtualText/benzrx1.htm#benz5)

The manner in which specific substituents influence the orientation of electrophilic substitution of a benzene ring is shown in the following interactive diagram (Figure 2.5). The product-determining step in the substitution mechanism is the first step, which is also the slow or rate determining step. Therefore, that there is a rough correlation between the rate-enhancing effect of a substituent and its site directing influence. The exact influence of a given substituent is best seen by looking at its interactions with the delocalized positive charge on the benzenonium intermediates generated by bonding to the electrophile at each of the three substitution sites.

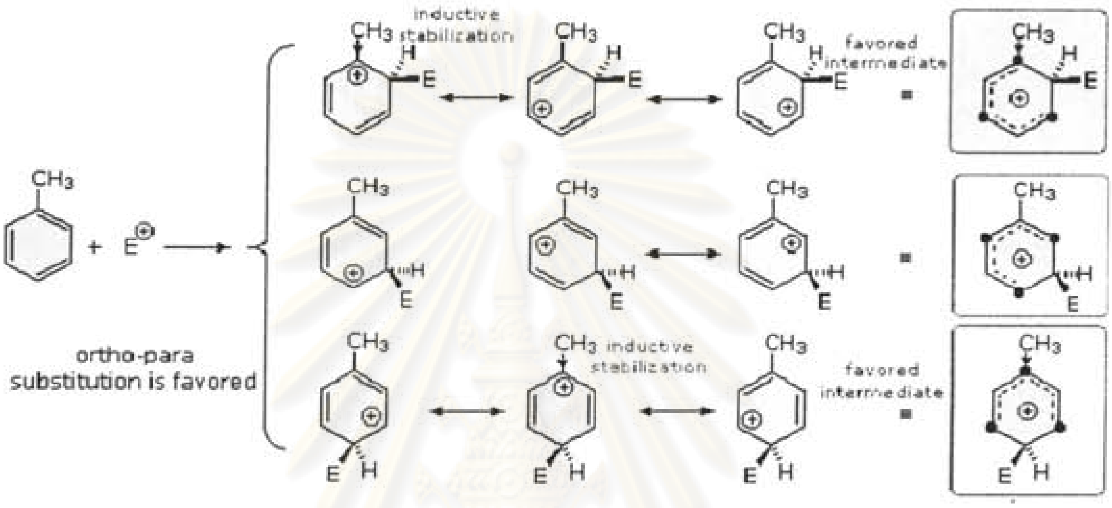


Figure 2.6 The delocalized positive charge on the benzenonium intermediates generated by bonding to the electrophile.
(www.cem.msu.edu/~reusch/VirtualText/benzrx1.htm#benz5)

From observations that led chemists to formulate an empirical classification of the various substituent groups commonly encountered in aromatic substitution reactions. Thus, substituents that activate the benzene ring toward electrophilic attack generally direct substitution to the ortho and para locations. With some exceptions, such as the halogens, deactivating substituents direct substitution to the meta location. The Table 2.1 summarizes this classification. The information summarized is very useful for rationalizing and predicting the course of aromatic substitution reactions, but in practice most chemists find it desirable to understand the underlying physical principles that contribute to this empirical classification. We have already analyzed the activating or deactivating properties of substituents in terms of inductive and resonance effects, and these same factors may be used to rationalize their influence on substitution orientation.

Table 2.1 Classification of the various substituent groups.

Orientation and Reactivity Effects of Ring Substituents				
Activating Substituents ortho & para-Orientation		Deactivating Substituents meta-Orientation		Deactivating Substituents ortho & para-Orientation
$-O^{(-)}$	$-NH_2$	$-NO_2$	$-CO_2H$	$-F$
$-OH$	$-NR_2$	$-NR_3^{(+)}$	$-CO_2R$	$-Cl$
$-OR$	$-NHCOCH_3$	$-PR_3^{(+)}$	$-CONH_2$	$-Br$
$-OC_6H_5$	$-R$	$-SR_2^{(+)}$	$-CHO$	$-I$
$-OCOCH_3$	$-C_6H_5$	$-SO_3H$	$-COR$	$-CH_2Cl$
		$-SO_2R$	$-CN$	$-CH=CHNO_2$

Theory of reactivity

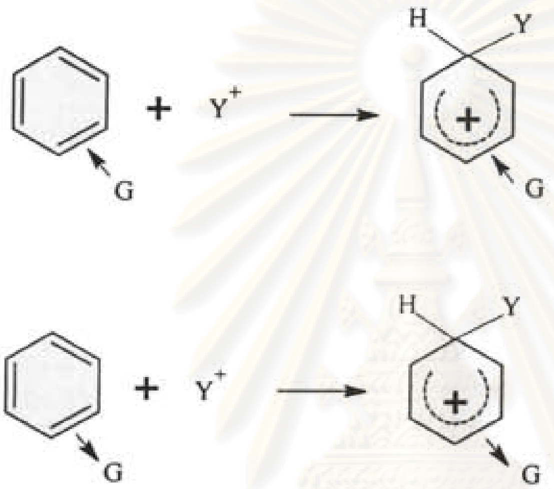
The activity of substituted benzene depends on type of substituent group. The group that releases electrons activates the ring is called "activating group". The group that withdraws electrons deactivates the ring called "deactivating group".

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 2.7 shows type of substituent group.



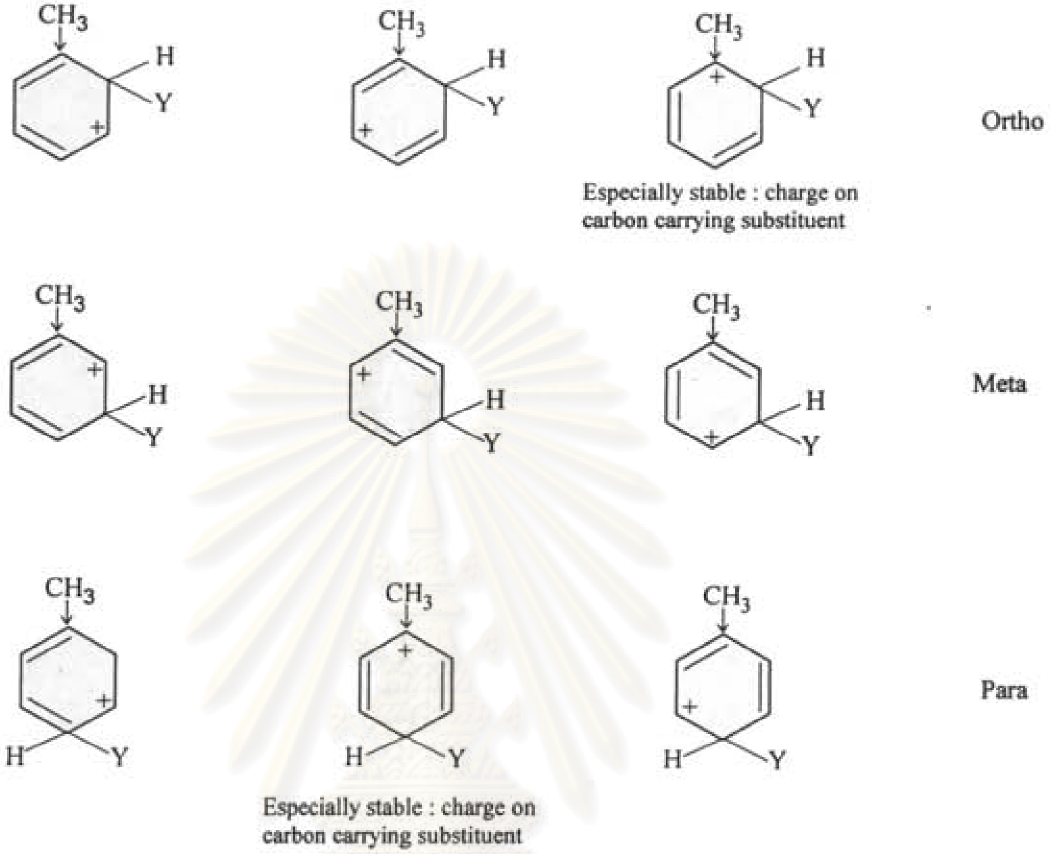
G = release electrons :
stabilizes carbocation,
activates

G = withdraws electrons :
destabilizes carbocation,
deactivates

Figure 2.7 Type of substituent group in electrophilic aromatic substitution

2.6. 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 2.8 activating group substituent at position *orho*, *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.

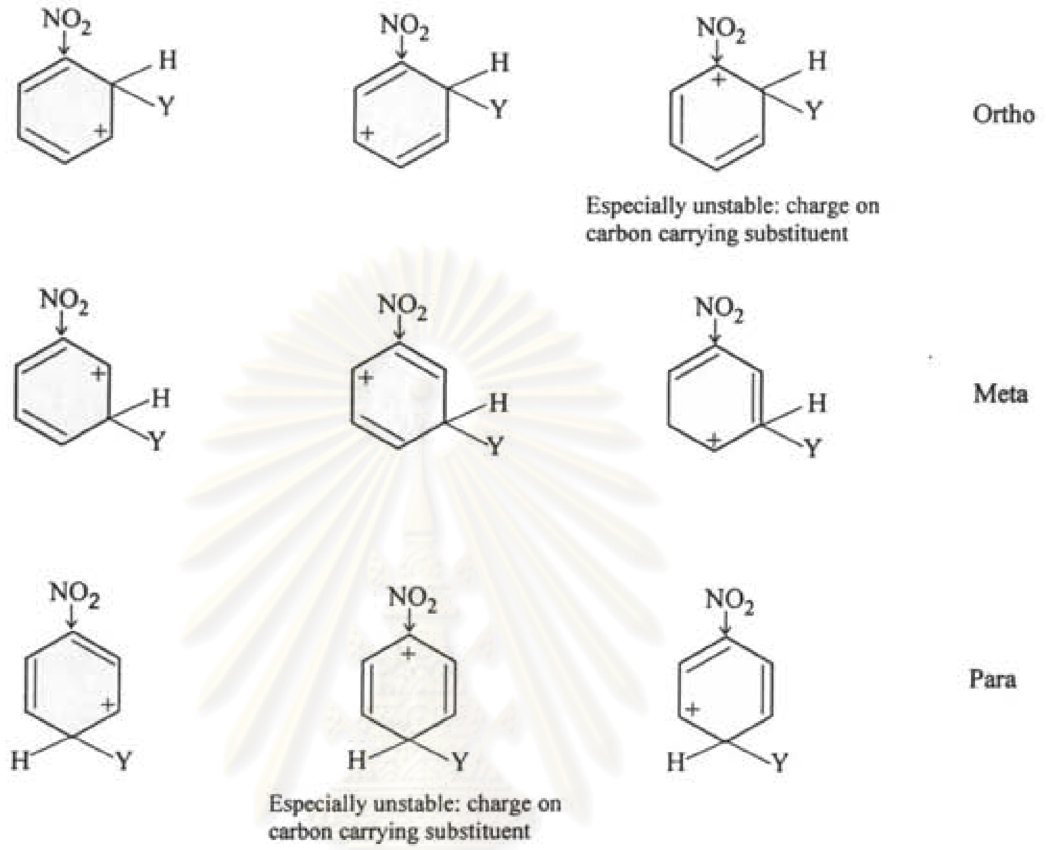


Especially stable : charge on carbon carrying substituent

Especially stable : charge on carbon carrying substituent

Figure 2.8 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 Figure2.9



Especially unstable: charge on carbon carrying substituent

Especially unstable: charge on carbon carrying substituent

Figure 2.9 Deactivating group substituent at position orho, para and meta

CHAPTER III

EXPERIMENTAL

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

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 Chemicals used in the catalyst preparation

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

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.

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			

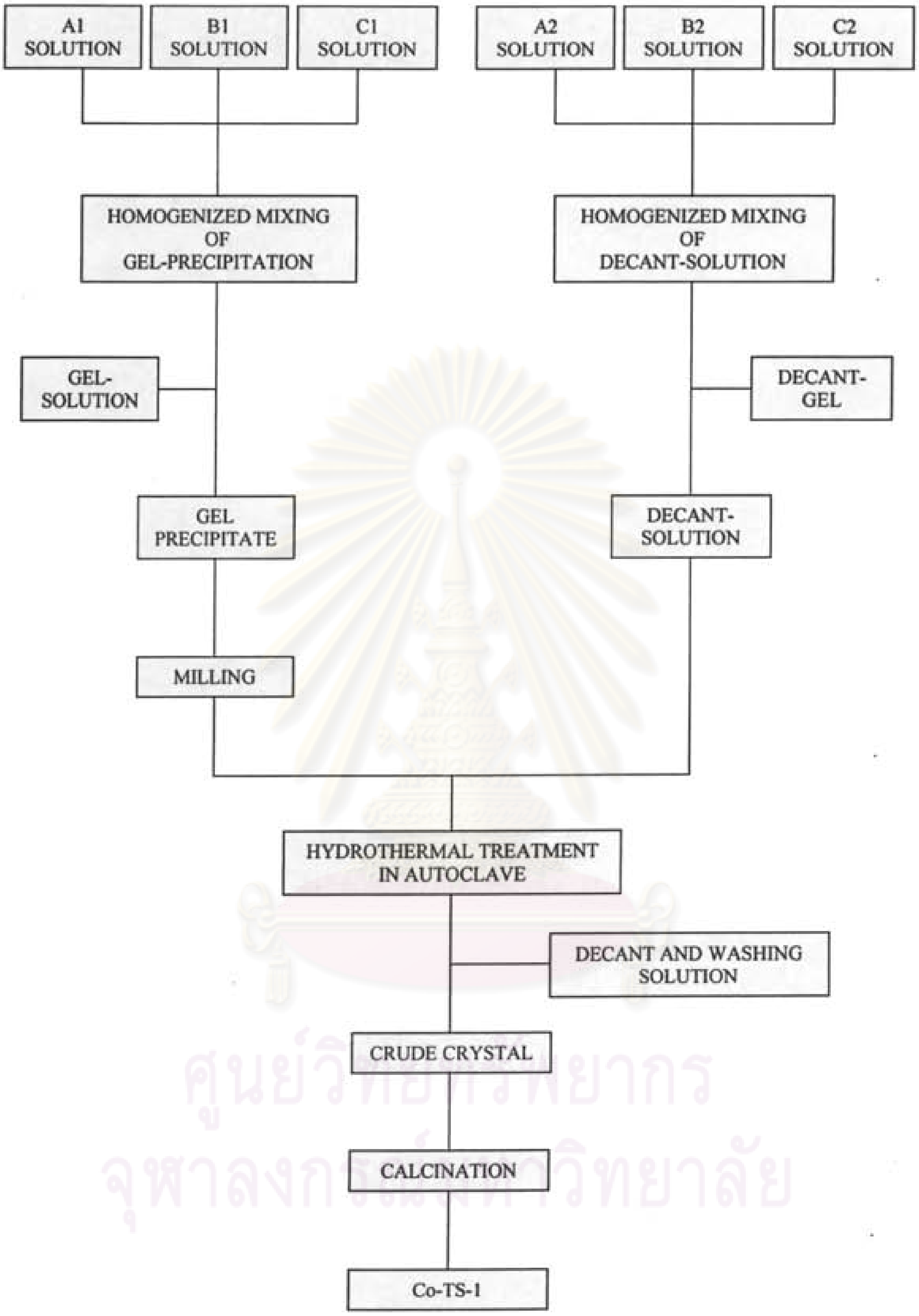


Figure 3.1 Preparation procedure of Co-TS-1 by rapid crystallization method.

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 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 and Silicon/Metal were set at 150, 200, 250 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 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 was maintained within the range 9-11 because this pH range is suitable for precipitation. H_2SO_4 (conc.) or KOH solution were used to adjust pH of the gel mixture to an appropriate level if it was necessary. The gel mixture was separated from the supernatant liquid by a centrifuge. The precipitated gel mixture was milled for totally 1 hour. The milling was done for 15 min and then the supernatant solution was removed by centrifugal separation before the hydrothermal treatment in order to obtain the uniform, fine crystals. The milling procedure was as follows: milled 15 min → centrifuge (to remove liquid out) 15 min → milled 15 min → centrifuge 15 min → milled 30 min → centrifuge 15 min.

Secondly, a decantation solution was prepared by adding solution A-2 and solution B-2 into solution C-2, same as for the preparation of gel mixture. The supernatant liquids from A-2, B-2 and C-2 were mixed together with the milled 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 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 3 days, followed by cooling the mixture to room temperature in the autoclave

3.1.2.3 Calcinations

The dry crystals were calcined in an air stream at 550 °C and held at that temperature for 7 h, by heating them from room temperature to 550 °C at a heating rate of 8.6 °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 Pretreatment catalysts

Co-TS-1 and TS-1 were placed into a round bottom flask then 5M of 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 at Scientific and Technological Research Equipment Centre, Chulalongkorn University.

3.2.2 BET surface area measurement

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

3.2.3 X-Ray Diffraction (XRD)

The crystallinity and X-ray diffraction patterns of the catalysts were performed by an X-ray diffractometer SIEMENS D5000 connected with a computer with Diffract ZT version 3.3 program for fully control of XRD analyzer. The experiments were carried out by using Cu Kα radiation with Ni filter. Scans were performed over the 2θ ranges from 6 ° to 40°.

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 were carried out using a flow apparatus. The catalyst sample (0.1 g) was treated at 550°C in helium flow for 1h and then saturated with 15 %NH_3/He mixture after cooling to 100 °C. After purging with helium at 100 °C for 1 h to remove weakly physisorbed NH_3, the sample was heated to 550 °C at therate of 10 °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 hydroxylation of Toluene

3.3.1 Chemicals

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

Table 3.3 The chemicals used for the reaction study.

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

3.3.2 Apparatus

The catalytic test was performed in a flow system shown diagrammatically in Figure 3.2. The reaction system consists of a reactor, a gas controlling system, an evaporating system, an oil bath and a gas chromatography. The instruments used in this system are listed and explained as follows:

3.3.2.1 Reactor

The reaction was performed in a conventional glass tubular reactor (inside diameter = 4 cm), at atmospheric pressure. The reactor consists of two parts (tube part and head part). The gas mixture entered to the reactor from the head part which is joined with a glass tube immersing in the mixture of catalyst and hydrogen peroxide in order to allow gaseous toluene flows upward from the bottom of the reactor.

3.3.2.2 The evaporating system

The evaporating system consists of a 1 meter tube bending in spiral shape. The entrance of the tube was installed with a three way valve which is connected to the gas controlling system in one side. Another side was adapted and used as the injection port. This tube was immersed in an oil bath which heated temperature at 150 °C and used as the evaporator for liquid alkyl benzene. The hot plate was used for heating up the oil bath. Liquid toluene was evaporated into gaseous phase before entering to the reactor by pulse injecting to the system via the injection port using a 1 ml syringe in order to control the accuracy of reactant amount.

3.3.2.3 Oil Bath

This instrument supplies the required heat to the reactor for the reaction. The reactor was operated at 70 °C.

3.3.2.4 Gas controlling system

The gas supplying system consists of a cylinder of ultra high purity nitrogen that equipped with a pressure regulator (0-120 psig), an on-off valve and a mass flow control was used for adjusting the flow rate.

3.3.2.5 Gas chromatography

The feed and products were analyzed by a gas chromatograph equipped with a FID detector (SHIMADZU GC9A). The operating conditions of the GC are listed in Table 3.4.

Table 3.4 Operating conditions for gas chromatograph

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

3.3.3 Reaction procedure

The hydroxylation of toluene with hydrogen peroxide was carried out by using a conventional bubble reactor shown in Figure 3.2 operated at atmospheric pressure.

The procedures are described in the detail below.

1) 1 g of catalyst powder, hydrogen peroxide and a magnetic bar were filled in the glass tube reactor.

2) Heating the reactor up to 90°C and kept at this temperature for 1 hour to remove gas from the pore of the catalyst.

3) Cool down the reactor to70 °C. Then, added water and H_2O_2 solution to adjust the final concentration of H_2O_2 solution in the reaction to a desired value.

4) Heat up the temperature of oil bath of the evaporating system to 150 °C.

5) Adjust the outlet pressure of nitrogen to 1.5 bars and turn on the on-off valve to allow nitrogen gas to pass through the evaporating system. The flow rate was adjusted to 60 ml/min by a mass flow controller. The outlet gas flow rate can be rechecked by using a bubble flow meter.

6) Start the reaction by injecting certain an amount of liquid toluene to the evaporating system. Upon entering the hot spiral tube, the liquid toluene was evaporated immediately to gaseous toluene and was flushed to the reactor by using N_2 as the carrier gas.

7) The gas mixture passes through the mixture containing the catalyst and hydrogen peroxide, where the hydroxylation of toluene reaction to took place.

8) The next period, the equivalent liquid toluene was injected into the toluene feed tube again.

9) Analyze the product sample by placing the reactor into the cool bath in order to stop the reaction.

10) Mix the liquid mixture with 40 ml of ethanol and stir until the liquid mixture became a homogeneous phase. After that, centrifuge the mixture in order to separate the catalyst from the liquid solution.

11) The liquid product was analyzed by the FID gas chromatography.
The chromatogram data were converted into mole of products using a calibration curve

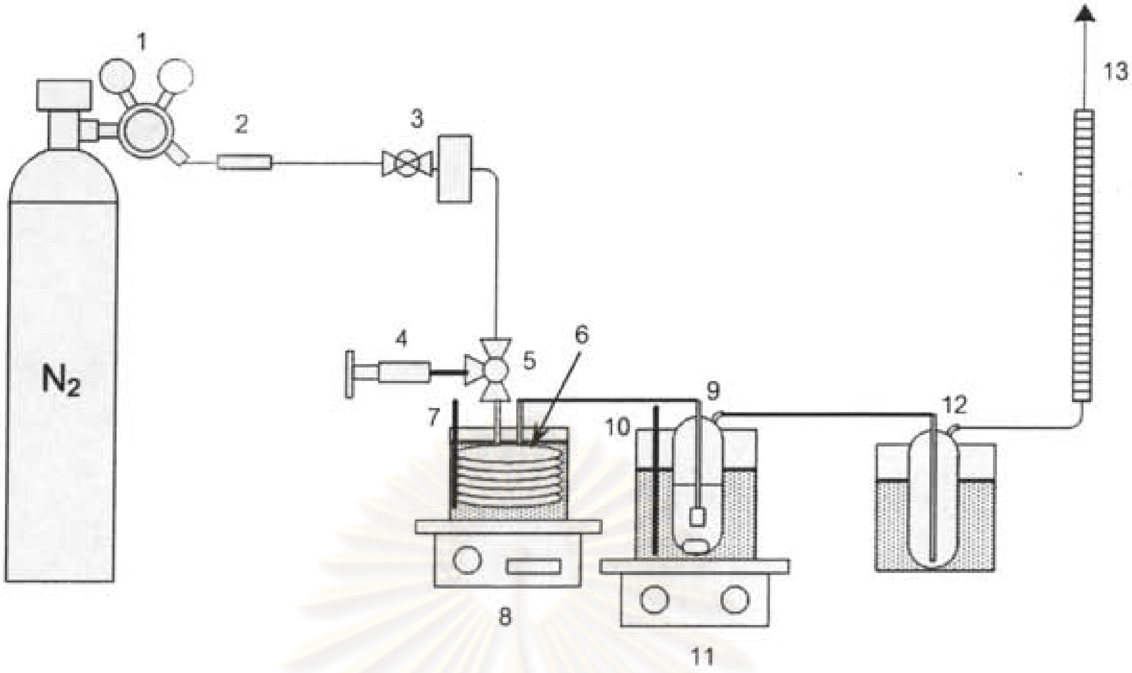


Figure 3.2 Schematic diagram of the reaction apparatus for the hydroxylation of toluene with hydrogen peroxide.

1. Pressure Regulator
2. Gas Filter
3. Gas Controlling System
4. Reactant Syringe
5. Three Way Connector
6. Evaporator
7. Thermometer
8. Oil Bath
9. Reactor
10. Thermometer
11. Oil Bath
12. Gas Trap
13. Vent Gas

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 product, selectivity and yield of products.

4.1. Catalytic characterization

The physical and chemical properties of Co-TS-1 and TS-1 were determined by several techniques to study the effects of catalytic behavior.

4.1.1 Chemical compositions

The chemical compositions of TS-1 and Co-TS-1 are determined by X-Ray Fluorescence Spectrometer (XRF) was used, for the quantitative determination of Co, Ti, and Si contents in the modified TS-1 sample. Since, the corporation of each cation (Si, Ti, Co) into the MFI structure is in random form. Therefore, it is impossible to fix the ratio of Si/Ti and Si/Co of the synthesized catalyst for each sample.

Table 4.1 Chemical compositions of the metals and the atomic ratio of Si/Ti and Si/Co of samples. (% by mole) before treatment

Sample	3 Day				1 Day			
	%Si	%Ti	%Co	Si/Ti	%Si	%Ti	%Co	Si/Ti
Co-TS-1(50)	94.26	3.62	1.11	26.00	95.34	2.40	1.35	39.71
Co-TS-1(150)	94.56	2.92	0.29	32.34	94.02	2.93	0.65	32.05
Co-TS-1(300)	94.86	2.68	0.43	35.28	94.24	3.26	0.48	37.01

Table 4.2 Chemical compositions of the metals and the atomic ratio of Si/Ti and Si/Co of samples. (% by mole) under treated

Sample	3 Day				1 Day			
	%Si	%Ti	%Co	Si/Ti	%Si	%Ti	%Co	Si/Ti
TS-1	97.34	2.61	none	37.29	98.00	1.95	none	50.25
Co-TS-1(50)	97.34	2.53	0.35	38.25	98.99	0.82	0.10	120.12
Co-TS-1(150)	97.09	2.40	0.17	40.37	97.33	2.26	0.10	42.90
Co-TS-1(300)	95.22	4.08	0.35	29.89	96.39	3.00	0.40	32.07

First, let consider the effect of aging time. Data in table 4.2 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.

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 in the MFI structure, Co-TS-1(before treatment) has cobalt cation higher than Co-TS-1(after treatment).In the case of Co-TS-1(after treatment),cobalt cation 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(after treatment).is lower than the amount of cobalt appears in Co-TS-1(before treatment)

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

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) before and after treatment is summarized in Figures 4.1 and 4.2 respectively. All recorded XRD patterns show six main characteristic peaks at 2 theta ≈ 8, 8.8, 14.8, 23.1, 24 and 26.7 which are typical for MFI structure [Taramasso et al., 1983], see section 2.1

Figures 4.1 and 4.2 show that MFI structure can well form within 1 day aging. Leaving the catalysts in the autoclave up to 3 days does not make any significant difference, which can be seen from a slight change of the XRD spectra.

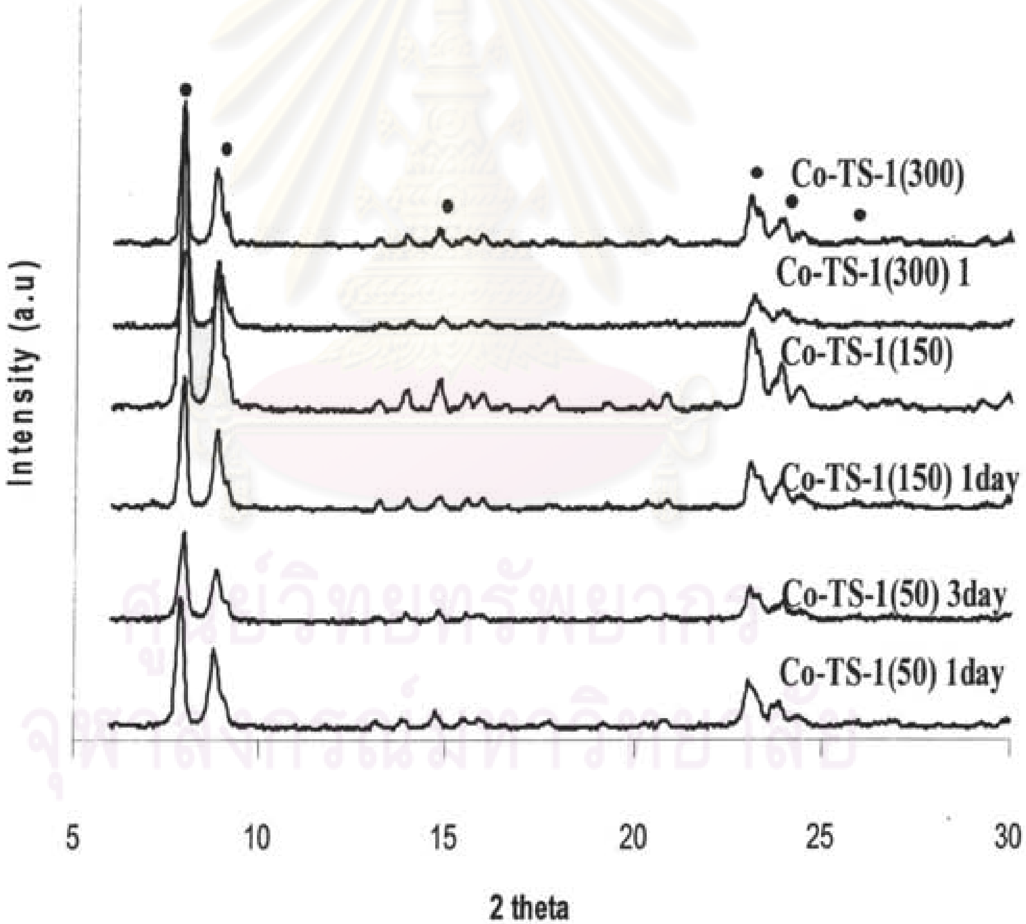


Figure 4.1 The XRD patterns of Co-TS-1 before treatment.

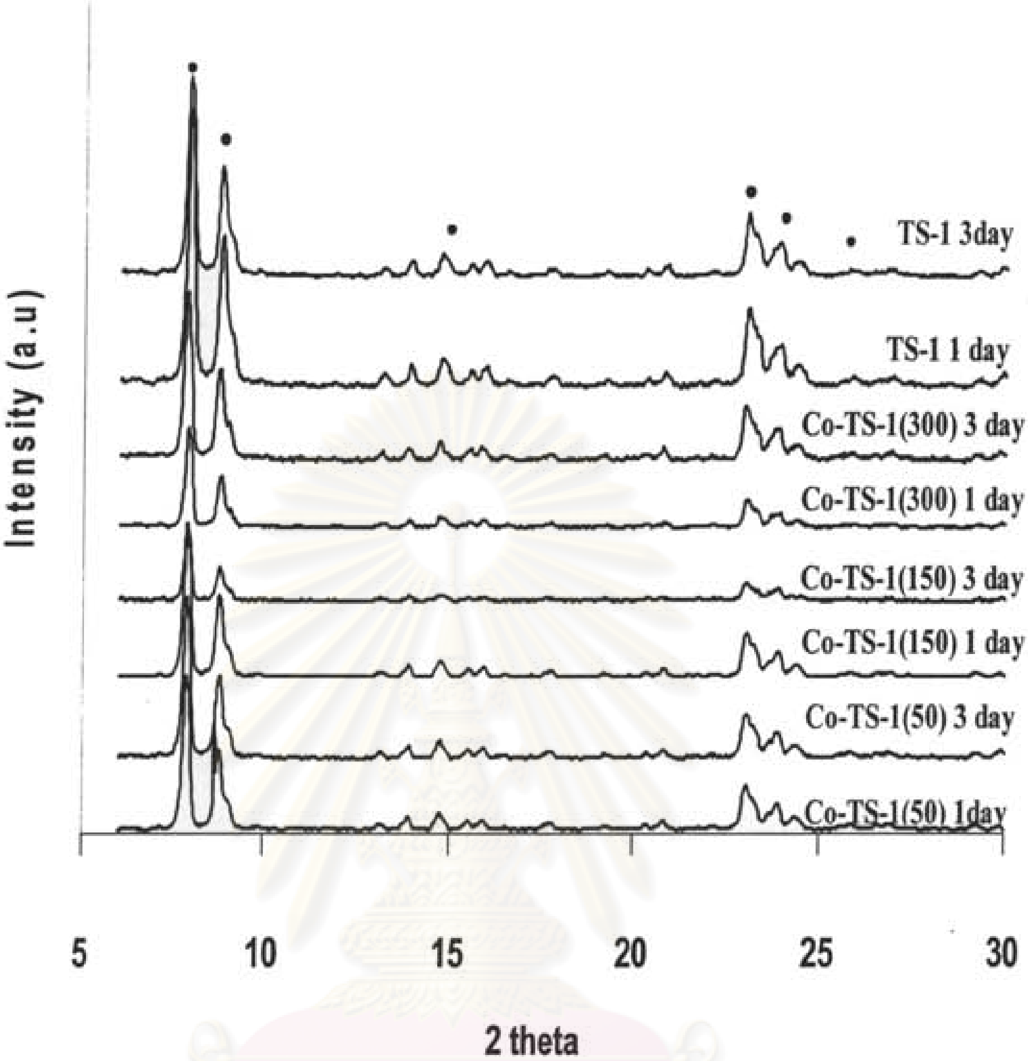


Figure 4.2 The XRD patterns of Co-TS-1 and TS-1 after treatment.

The appearance of the peaks at 2 theta ≈ 24 and 26.7 indicate an orthorhombic symmetry which is typical for TS-1 having titanium cation (Ti^{4+}) with in the framework of TS-1 having Si/Ti < 100 [Grienisen et al.,2000]. The peaks at 2 theta ≈ 24 and 26.7 are also interpreted as a change from a monoclinic symmetry (silicalite) to a more catalytic active orthorhombic symmetry (Titanium silicalite) [Taramasso et al.,1983]. The absence of the peak at 2 theta ≈ 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].

4.1.3 Location of titanium cation

The location of Ti^{4+} in the catalyst can be determined using the absorption of infrared technique. It has been reported that Ti^{4+} embedded in the MFI framework would produce an IR absorption band around 960 cm^{-1} [Liu et al.,2005 and Bengoa et al.,1998]. The characteristic absorption bands of Ti^{4+} in the TS-1 and modified TS-1 catalysts are presented in Figure 4.3. All samples have the absorption band at 960 cm^{-1} which indicates that all catalysts have Ti^{4+} incorporated in the framework of TS-1 zeolite

It should be repeated here that the catalytic performance of TS-1 was claimed to be related to the amount of Ti on the framework of zeolite [Liu et al.,2006].

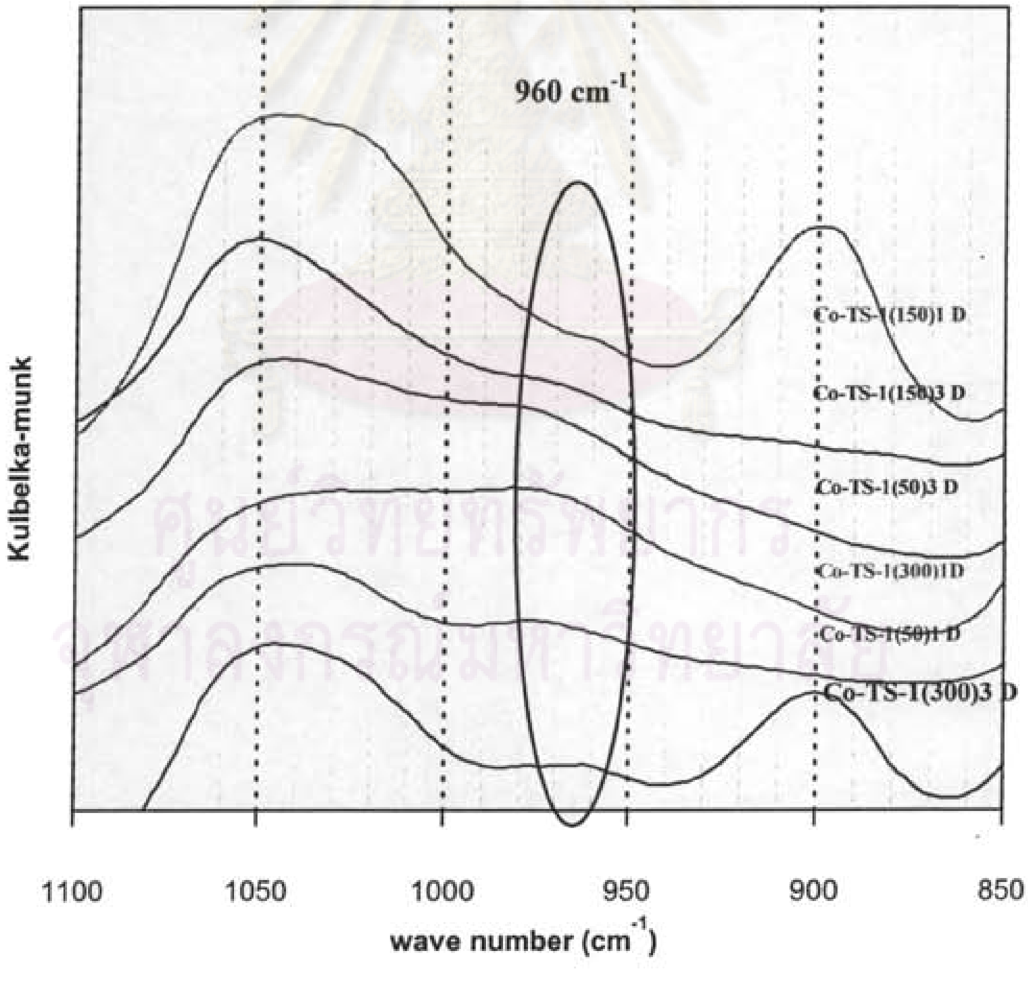


Figure 4.3 IR spectra of Co-TS-1 before treatment.

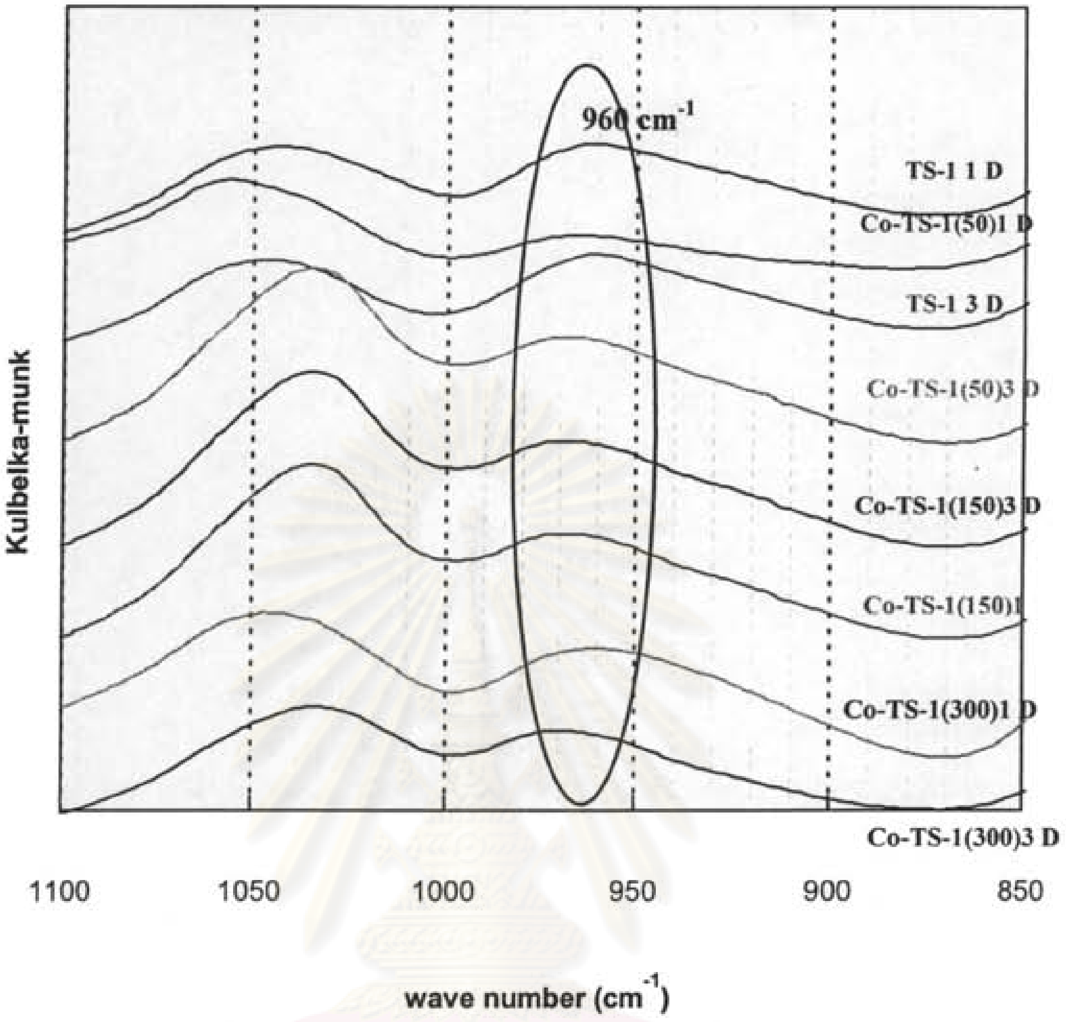


Figure 4.4 IR spectra of Co-TS-1 and TS-1 after treatment.

4.1.4 Surface Area

The surface areas of Co-TS-1 and TS-1 samples are presented in Table 4.3. All Co-TS-1 samples have surface area in the range 260-315 m^2/g which is not so different. The exception in Co-TS-1(150 N 3) which has surface area 394 m^2/g Hence, any different observed during catalytic testing should not be the result of the difference in catalyst surface area.

Table 4.3 Composition and surface area of Co-TS-1 and TS-1 samples.

Sample	**A_{BET} (m^2/g)**			
	With treatment		**No treatment**	
	1 day	**3 day**	**1 day**	**3 day**
TS-1	-	-	341	344
Co-TS-1(50)	311	314	309	288
Co-TS-1(150)	258	394	257	286
Co-TS-1(300)	282	304	284	267

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 selective hydroxylation of toluene performed in a typical bubble reactor over TS-1 and Co-TS-1 are discussed in this section. Since the main interest of this reaction is to maximize the usage of H_2O_2, the amount of H_2O_2 that reacts with toluene and converts toluene to organic products is much more concern. Therefore, the H_2O_2 conversions to organic compounds are reported in this chapter instead of the total conversion of H_2O_2, which must include the decomposition of H_2O_2.

Before discussing the reaction results, let have a look at mixing phenomena occurring in the reactor first. In the bubble reactor, a catalyst is put into an appropriate of water. Then the reactor is heated up to 90 °C to remove gas from the pore of the catalyst and fill the pore with water. Then the reactor is cooled down to the reaction temperature, 70 °C. Next, 30 wt% H_2O_2 aqueous solution and additional water (if necessary) are added to adjust the concentration of H_2O_2 to a desired value.

It is well known that several cations can accelerate the decomposition reaction of H_2O_2. The rapid decomposition can lead to a dangerous situation. Because of this reason, an upper limit concentration of H_2O_2 that can run the reaction safely must be determined. To determine the upper limit concentration of H_2O_2, several H_2O_2 solutions having different concentrations were prepared. Then, the catalyst is put into the prepared H_2O_2 solutions at room temperature. The decomposition of H_2O_2 can be observed from the formation of gas bubbles which are the decomposition product. The severity of the decomposition reaction can be evaluated from the rate of bubble generation i.e. the faster the bubbles generate, the more severe the decomposition reaction.

It is found that all catalysts can be run safely at H_2O_2 concentration not more than 7.5 wt%, though some catalysts can be used at higher H_2O_2 concentration. Because of this reason, the highest concentration of H_2O_2 in the present work is limited at 7.5 wt%.

Before toluene vapor is fed to the reactor, the catalyst surface is covered with water and H_2O_2. When nitrogen carrier gas is bubbled through the H_2O_2 solution in the reactor, toluene vapor in the carrier gas would dissolve into the aqueous phase. Due to the solubility of toluene in water is rather low, this factor should play some roles in controlling the reaction rate by limiting the concentration of toluene in the aqueous phase. In addition the dissolved toluene must present on the catalyst surface before the hydroxylation reaction can occur. The concentration of toluene on the catalyst surface which depends on the concentration of dissolved toluene, therefore, should also plays some roles in controlling the reaction rate.

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

4.2.1 The hydroxylation of toluene

The catalytic activity of toluene hydroxylation over the synthesized catalysts (TS-1 and Co-TS-1) with hydrogen peroxide concentrations 7.5 wt% and 3 wt% in water are summarized in Table 4.4

The total volume of hydrogen peroxide solution in the reactor used in each run is 40 ml which is equal to 0.38 mol and 0.13mol for the 7.5 and 3 wt% solutions, respectively. The total amount of toluene used in each run is 1.5 ml (0.0141 mol). It is important to note here that the total amount of toluene said above is the amount of toluene fed to the reactor with the gas bubble. Because of this reason, the real mole of toluene in the solution which can react with hydrogen peroxide is much lower than the mole of hydrogen peroxide presents in the solution (i.e. the ratio of mole toluene per mole H_2O_2 << 1).

Table 4.4 Comparison of the catalytic performance of various catalysts before treatment and after treatment

Co-TS-1	Aging Day	Ratio Si/Co	wt% H_2O_2	% conversion H_2O_2	% Selectivity		
					Benzaldehyde	*o*-cresol	*p*-cresol
Treated	3	50	7.5	0.0192	85.67	14.33	0
			3	0.0691	89.93	10.07	0
		150	7.5	0.0299	62.42	23.04	14.53
			3	0.027	0	80.91	19.09
		300	7.5	0.0377	69.25	12.72	18.01
			3	0.0186	45.35	42.46	12.18
	1	50	7.5	0.0877	90.67	9.33	0
			3	0.0467	66.17	33.83	0
		150	7.5	0.0505	60	40	0
			3	0.1896	0	63.38	36.62
		300	7.5	0.0178	86.89	13.10	0
			3	0.0394	89.27	10.72	0
No treatment	3	50	7.5	0.0093	85.67	14.32	0
			3	0.0192	13.02	61.7	25.28
		150	7.5	0.0106	0	76.088	23.92
			3	0.0913	0	63.385	36.614
		300	7.5	0.0054	29.36	39.38	31.24
			3	0.0048	0	71.58	28.42
	1	50	7.5	0.0141	46.29	38.47	15.23
			3	0.0422	83.59	16.41	0
		150	7.5	0.0089	22.14	28.24	49.60
			3	0.0083	0	100	0
		300	7.5	0.0075	56.99	43.01	0
			3	0.023	14.87	9.91	75.21

Since the main interest of this work is the production of cresol, any catalyst has high cresol selectivity will be considered. From this point of view and data shown in table 1, the catalysts that satisfy the above criterion are 150 T 3, 150 T 1, 150 N 3, 150 N 1 and 300 N 3. (Due to its 150 T 3 has basis Co-TS-1 Si/Co 150 after treatment and cave 3 day, 150 T 1 has basis Co-TS-1 Si/Co 150 after treatment and cave 1 day, 150 N 3 has basis Co-TS-1 Si/Co 150 before treatment and cave 3 day,150 N 1 has basis Co-TS-1 Si/Co 150 before treatment and cave 1 day, 300 N 3 has basis Co-TS-1 Si/Co 300 before treatment and cave 1 day) The remainders will not be discussed any more from this point forward.

It should be reminded here that the amount of H_2O_2 required for the formation of benzaldehye is twice the amount of H_2O_2 required for the formation of the same mole of cresol. Therefore, it can be hypothesized that the higher the concentration of H_2O_2 used, the higher the amount of benzaldehyde produced. It can be clearly seen that data exhibit in Table 1 support this hypothesis. All catalysts produce only cresols (both ortho and para isomers) at H_2O_2 concentration 3wt%. When the concentration of H_2O_2 is increased from 3wt% to 7.5wt%., all catalysts, but 150 N 3, loss cresol selectivity via the occurrence of benzaldehyde.

Before discussing the catalytic activity, one should be kept in mind that the conversion reported is the conversion of H_2O_2 to organic products (benzaldehyde, o-cresol and p-cresol), not the total conversion of H_2O_2 which must include the decomposition of H_2O_2. From this point forward, unless otherwise stated, the H_2O_2 conversion means the conversion of H_2O_2 to organic products. In addition, each experiment used the same amount of toluene but the amount of H_2O_2 used is varied.

To examine the experimental results using H_2O_2 conversion alone, may lead to misinterpretation of the experimental results. Therefore, the productivities of the organic products are also provided to give a clearer view of the results. For example, let consider the catalysts 150 T 3, 300 N 3, and 150 N1. These catalysts, when the concentration of H_2O_2 is increased from 3wt% to 7.5 wt% (2.5 time increase), the observed H_2O_2 conversions are slightly increased. The productivities data, however, give different picture. When the concentration of H_2O_2 is increased 2.5 time, the amount of organic products produced also increased about 2 times. The increase amount of organic products formed, however, mainly belongs to benzaldehyde which is not the required product. These results agree with what is expected before that the increase in H_2O_2 concentration will result in the increase in benzaldehyde formation rather then the formation of cresol.

150 T 1 and 150 N 3 behave differently when the concentration of H_2O_2 is increased from 3wt% to 7.5 wt%. Both catalysts cause H_2O_2 to decompose more than the others, thus results in lower H_2O_2 conversion when the concentration of H_2O_2 is increased from 3wt% to 7.5wt%. At high H_2O_2 concentration (7.5wt%), the catalyst 150 T 1 losses the selectivity towards cresols via the occurring of benzaldehyde. The catalyst 150 N 3, though, does not produce any detectable benzaldehyde at 7.5wt% H_2O_2 concentration, this catalyst causes the most severe decomposition of H_2O_2 as can be seen from the largest amount of gas bubbles generated during the reaction.

Reaction study reveals that the treatment of the catalysts can makes the catalyst more active for the hydroxylation reaction and less active for the decomposition of H_2O_2. The lower the concentration of H_2O_2, the lower the loss of H_2O_2 due to its own decomposition and the formation of the unwanted product (benzaldehyde). It suggests that the treatment, washing with nitric acid solution, removes some species that may block the selective site for the hydroxylation. That species also enhances the decomposition of H_2O_2 which is not wanted.

To determine which parameters affecting the activity and selectivity of the catalysts, additional characterization, NH_3-TPD, is performed. It should be noted here that NH_3-TPD can give a different view from XRF. While XRD inform the total contents of cations of the catalyst, NH_3-TPD can give information which can be related to the amount of cations locate on the surface accessible by the reactant. Since the surface of TS-1 is hydrophobic in nature, the amount of Bronsted acid site (-OH) should be low. It may be possible to assume that all NH_3 adsorb on the Lewis acid site (the cation).

The results obtained from NH_3-TPD suggest that the catalytic activity and selectivity towards cresol and/or benzaldehyde has some relation with the acidic strength of the catalyst. Too high acid strength (for example, due to the contamination of Al^{3+} in the catalyst structure) will make the catalyst more active but less selective for cresol. In addition, catalysts having too high acid strength also causes a rapid decomposition of H_2O_2. The source of aluminiun cation that contaminates the catalyst has yet to be determine.

Finally, it can be concluded that addition of Co in an appropriate amount can improve the activity and selectivity of TS-1 for the hydroxylation of toluene to cresols. However, a better care must be taken to avoid contamination of unexpected cations which may manipulate the catalytic behaviors and causes unwanted results.

4.3 The importance of the 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.

Let consider the NH_3-TPD spectra, It is found that NH_3-TPD profile 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 290 - 310°C. The profile is showed in Figure 4.7 and 4.11. The NH_3-TPD of TS-1(3 day), and TS-1(1 day) are demonstrated in Figure 4.5-4.6. They can be deconvoluted into three peaks. They have special peak which unmodified TS-1 does not exist that is peak around 190 – 214°C will be named here "the medium strength acid site". This peak possibly effect to catalytic activity of catalyst.

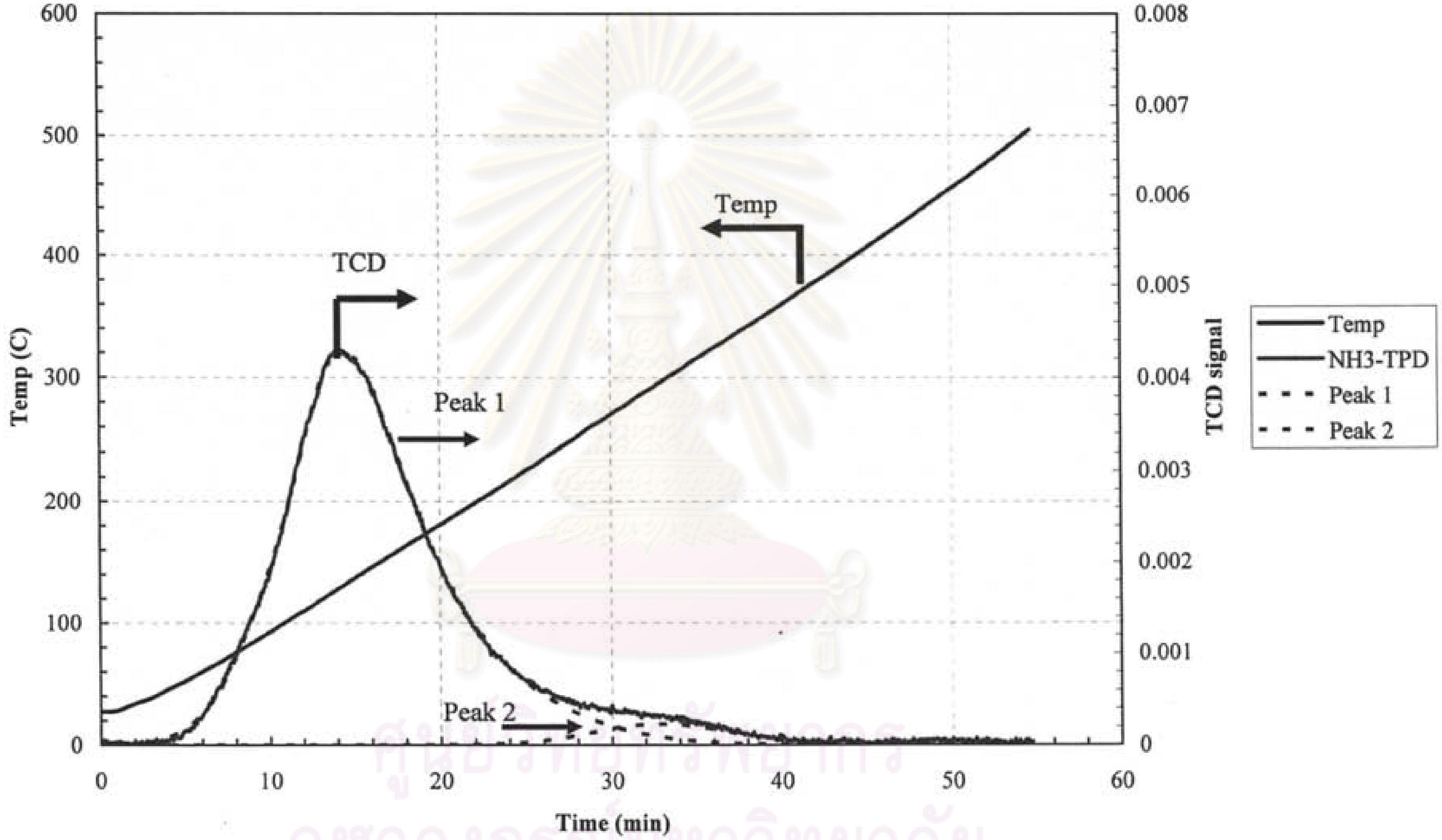


Figure 4.5 NH$_3$-TPD of TS-1(3 Day)

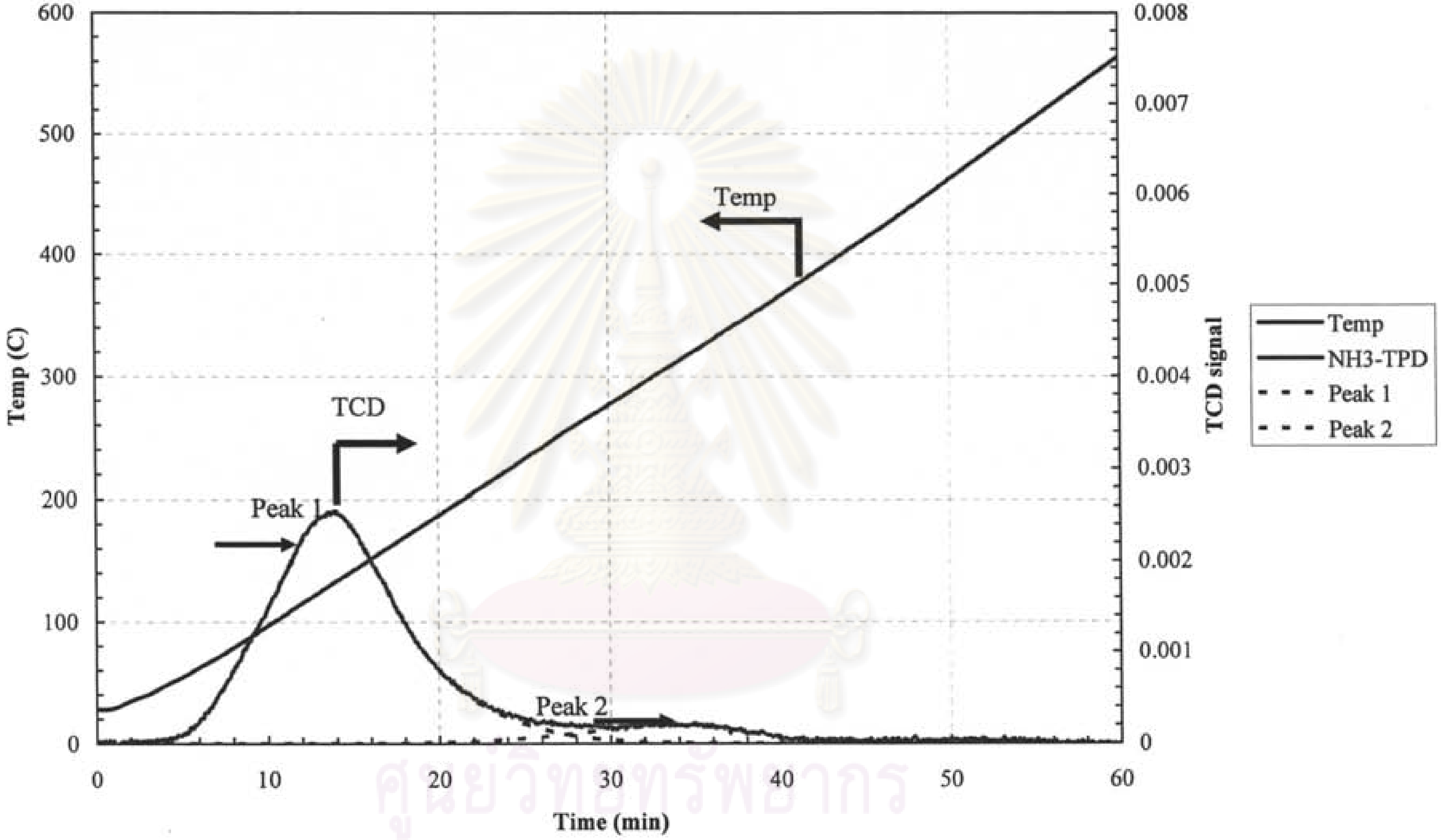


Figure 4.6 NH$_3$-TPD of TS-1(1 Day)

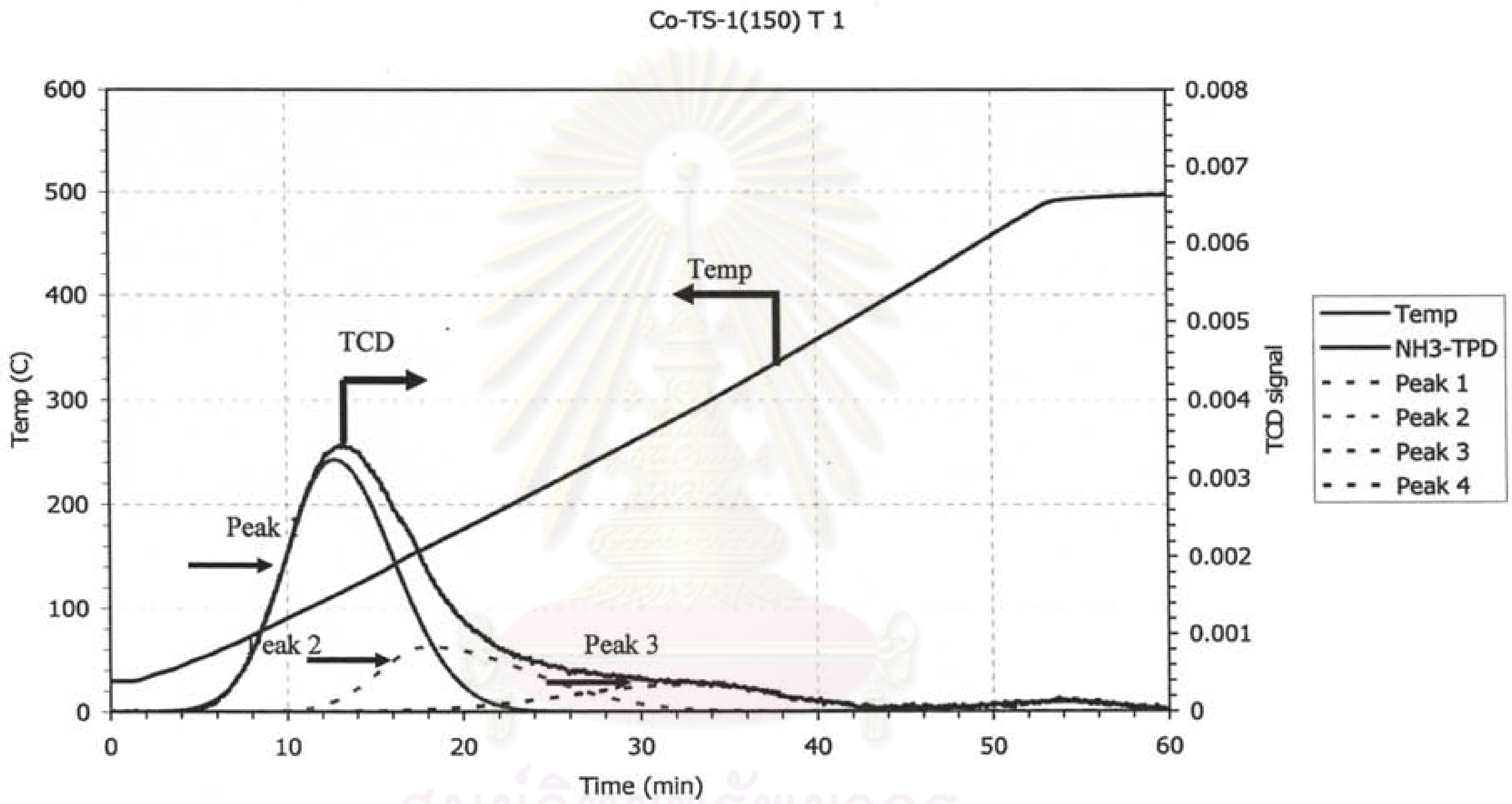


Figure 4.7 NH$_3$-TPD of Co-TS-1(150 T 1)

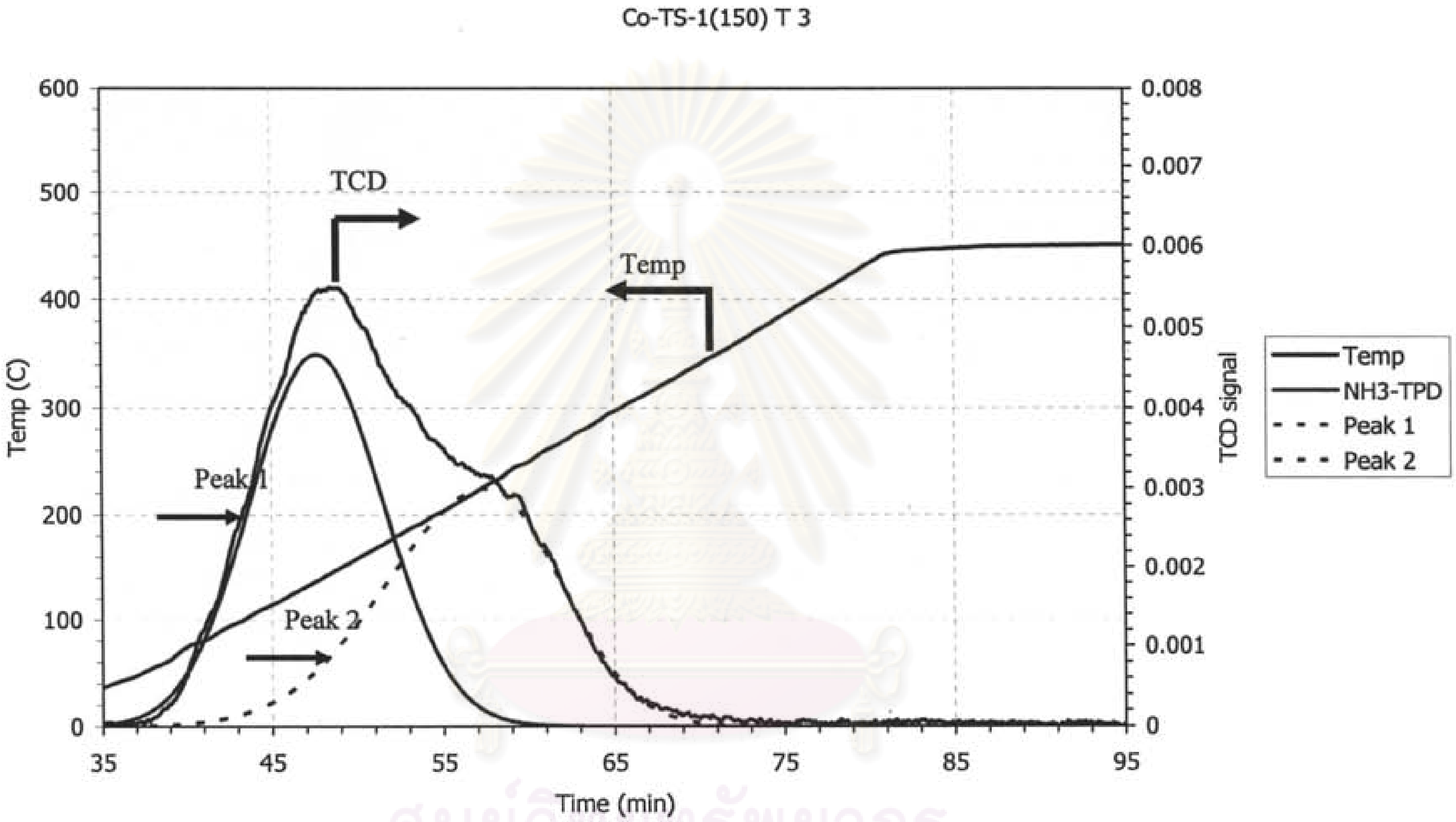


Figure 4.8 NH_3-TPD of Co-TS-1(150 T 3)

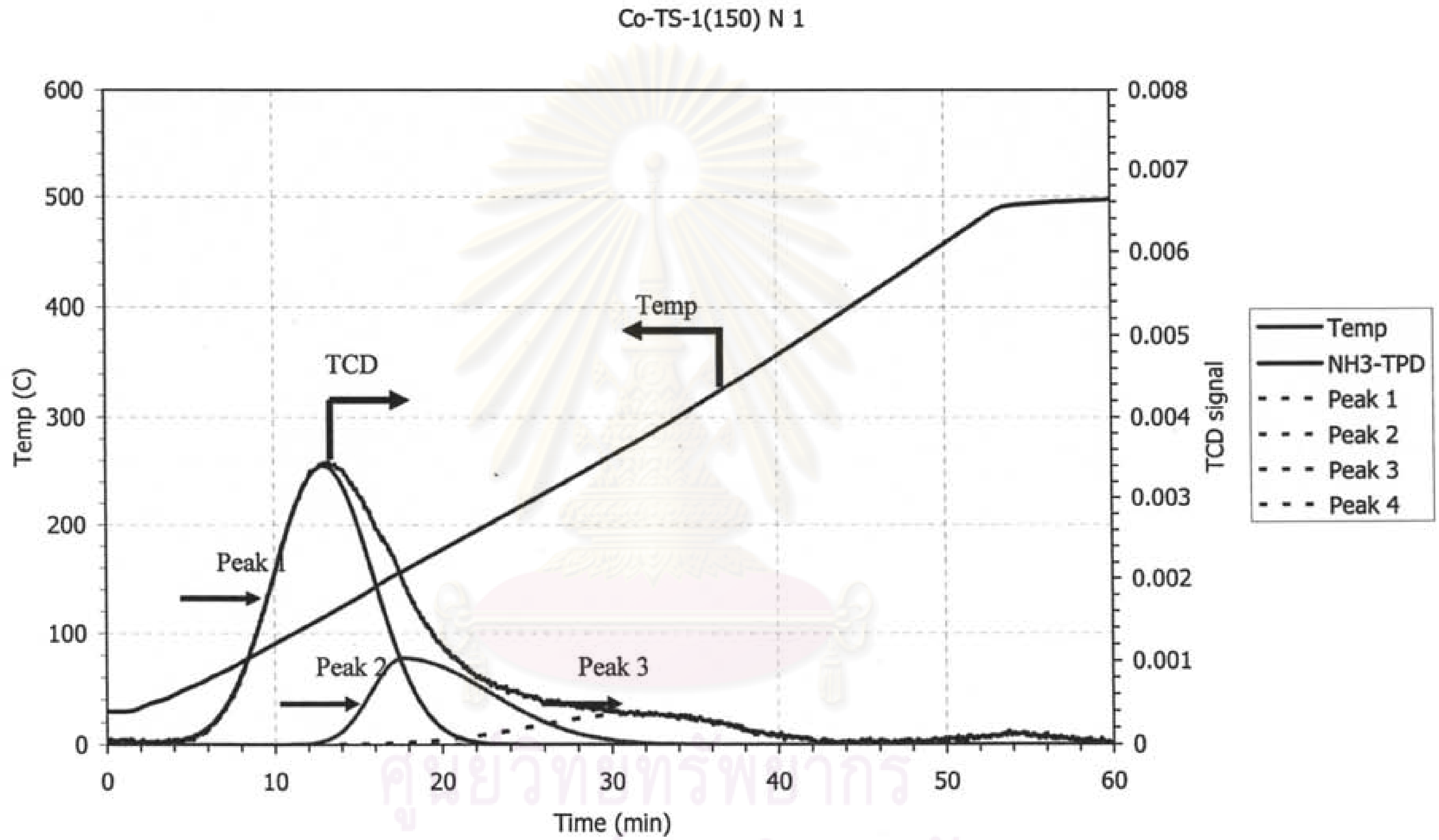


Figure 4.9 NH_3-TPD of Co-TS-1(150 N 1)

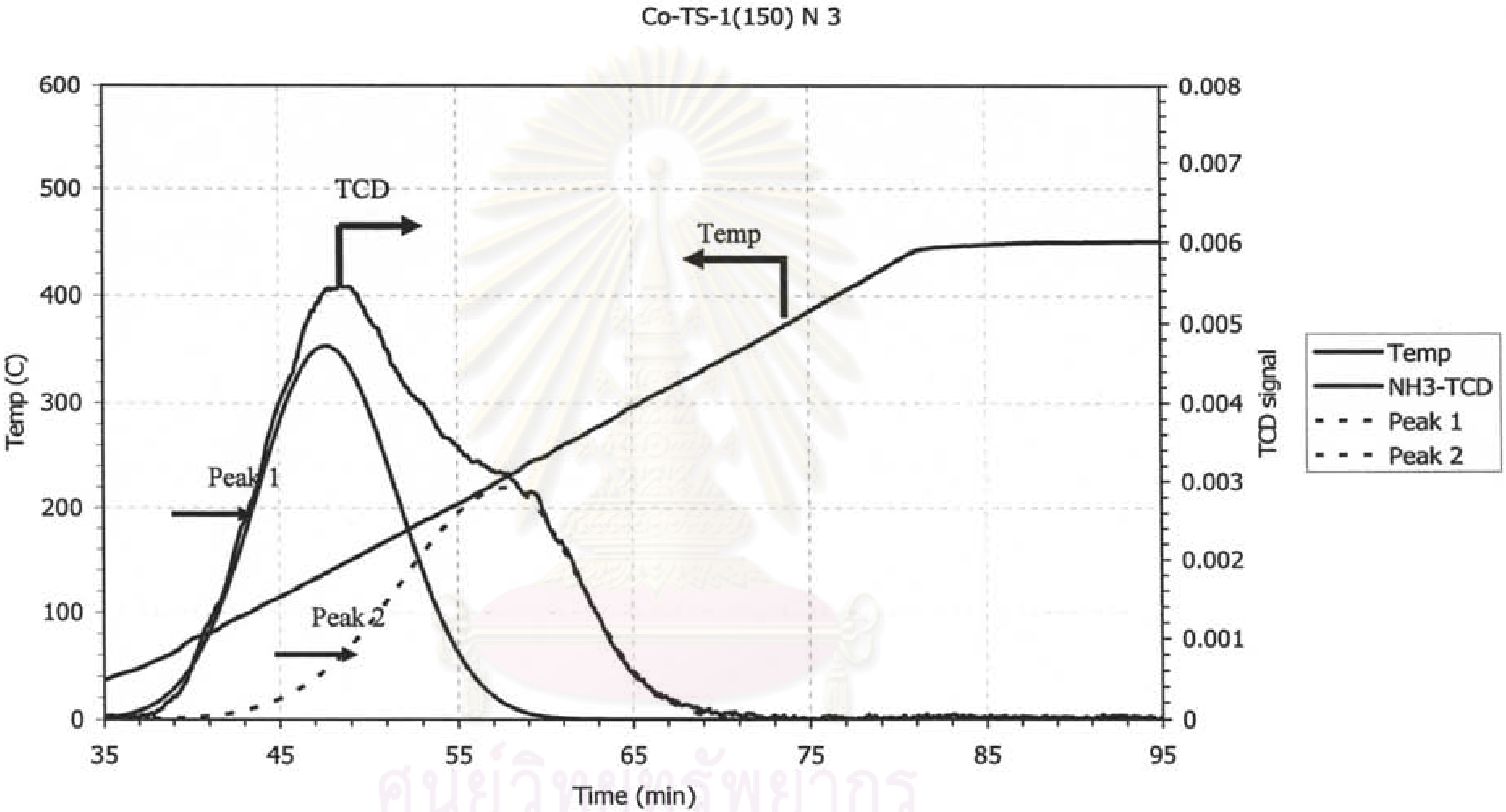


Figure 4.10 NH$_3$-TPD of Co-TS-1(150 N 3)

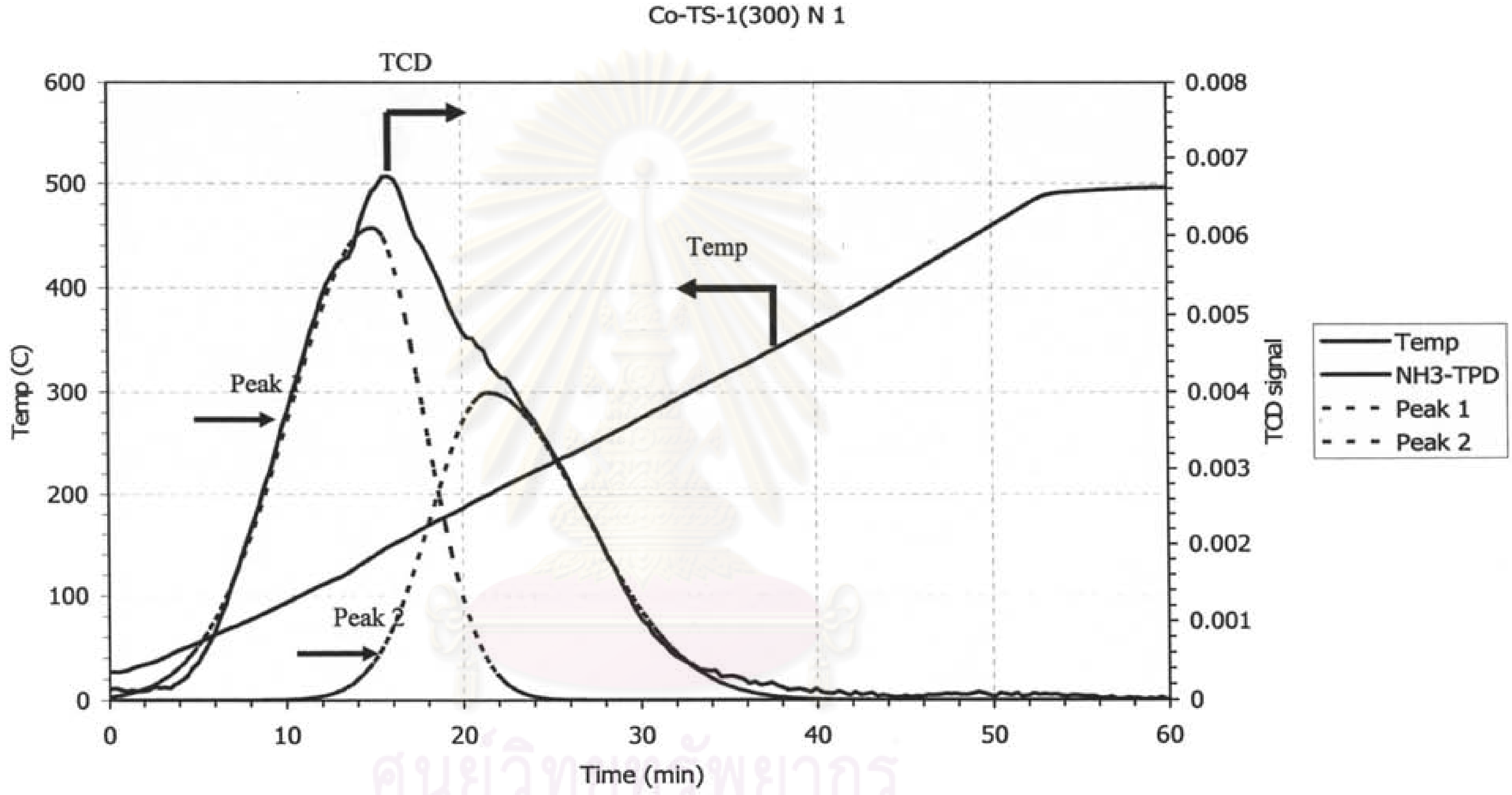


Figure 4.11 NH_3-TPD of Co-TS-1(300 N 3)

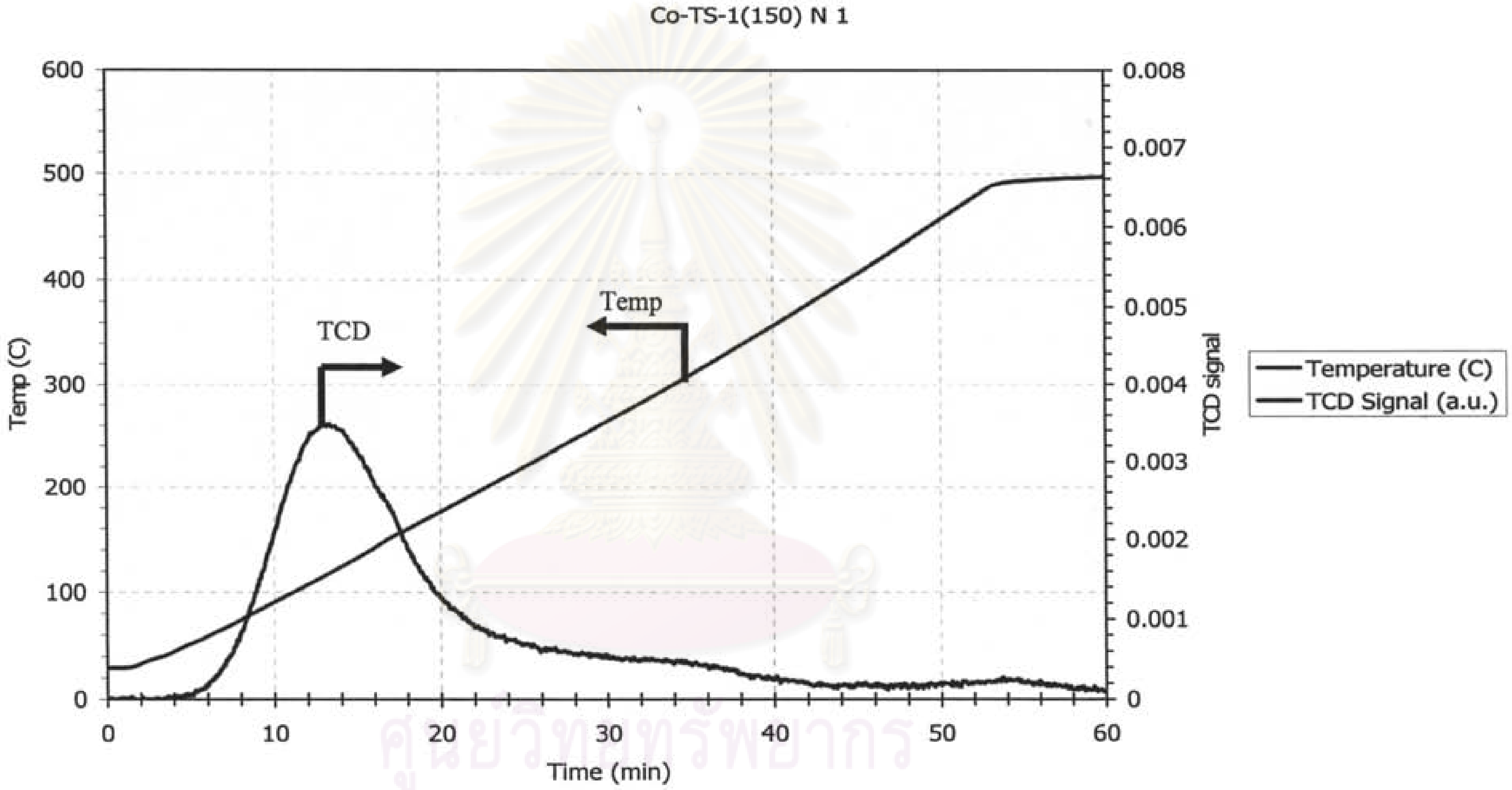


Figure 4.12 NH_3-TPD of Co-TS-1(150 N 1)

Table 4.5 Productivity of catalysts before treatment and after treatment at 7.5 wt% H_2O_2

sample	(%)conversion	Product ($x10^{-13}$)(mole)		
		Benzaldehyde	o-cresol	p-cresol
150 Co-TS-1 3D NO	0.0106	0	3.66	1.15
150 Co-TS-1 3D treat	0.0299	16.5	0.6	0
150 Co-TS-1 1D NO	0.0089	1.45	0.92	1.63
150 Co-TS-1 1D treat	0.0505	2.29	0.76	0
300 Co-TS-1 3D NO	0.0054	1.11	0.74	5.92

Table 4.5 Productivity of catalysts before treatment and after treatment at 3 wt% H_2O_2

sample	conversion (%)	Product ($x10^{-13}$)(mole)		
		Benzaldehyde	o-cresol	p-cresol
150 Co-TS-1 3D NO	0.0398	0	2.05	0.87
150 Co-TS-1 3D treat	0.0270	0	3.95	0.93
150 Co-TS-1 1D NO	0.0083	0	1.51	0
150 Co-TS-1 1D treat	0.0913	0	1.05	6.06
300 Co-TS-1 3D NO	0.0048	0	0.62	0.24

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 4.13. 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 4.13.

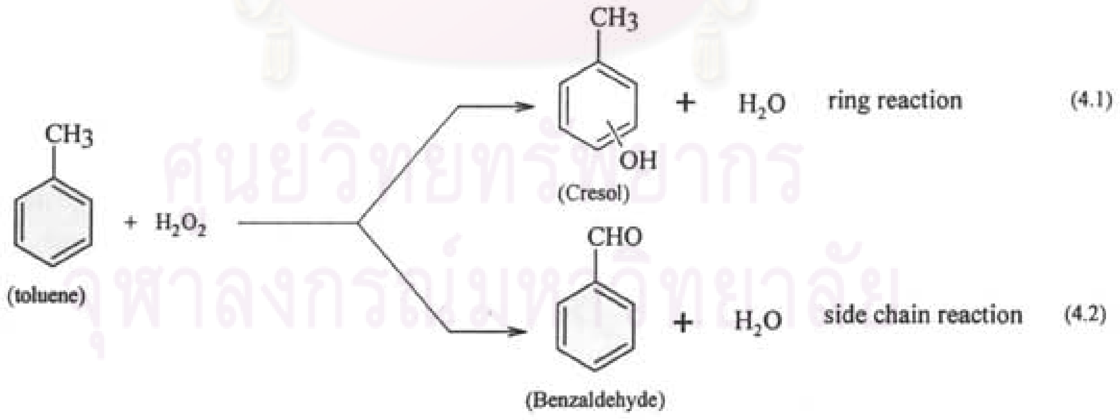


Figure 4.13 The two parallel reactions of hydroxylation of toluene.

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

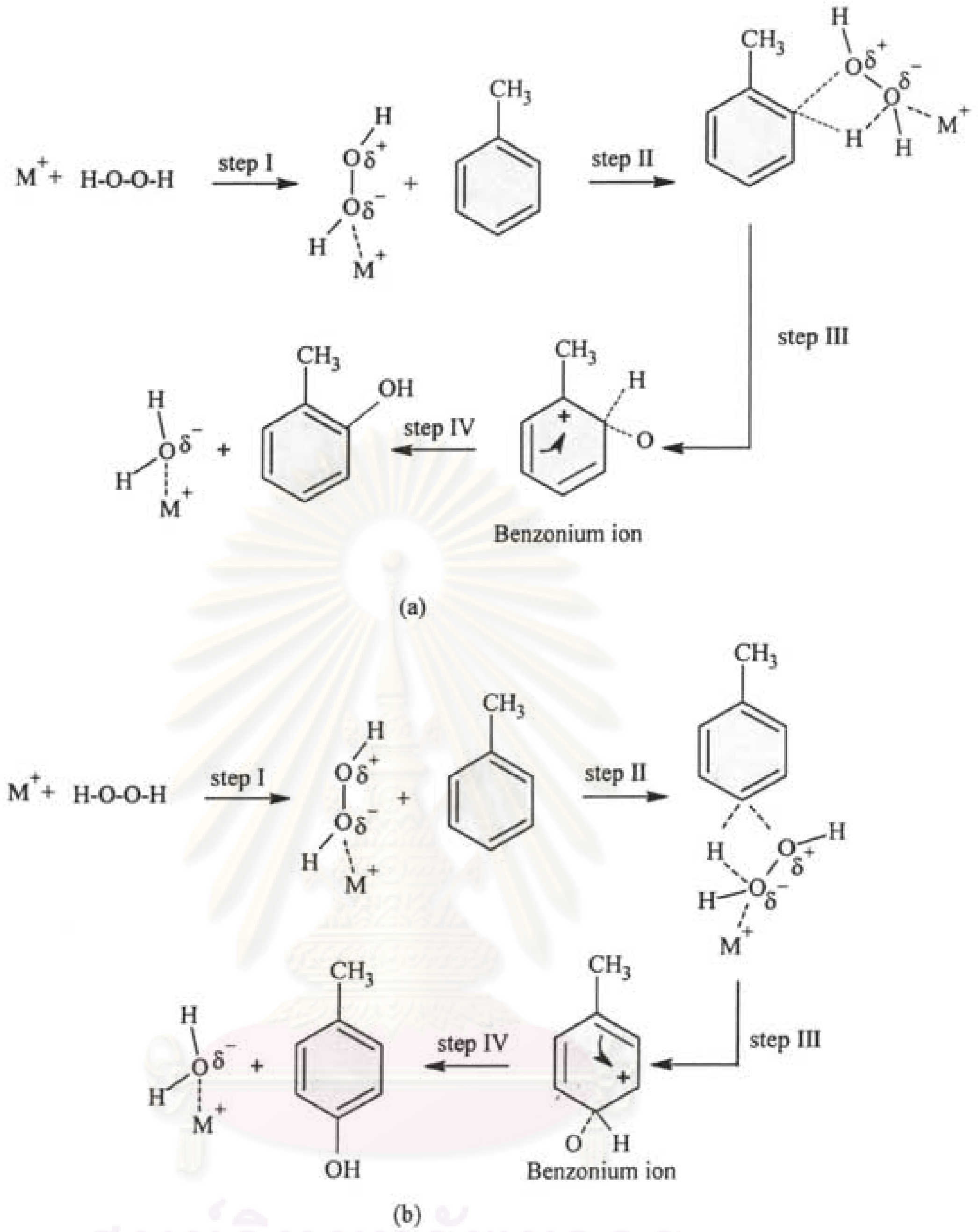
The mechanism for the formation of o-cresol and p-cresol are showed in Figure 4.14. The mechanism of cresol is proposed to consist of the following four steps:

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

4.4.2 Proposed reaction scheme for the oxidation at the methyl group

The reaction scheme of benzaldehyde formation is expected to be different from the mechanism of cresol formation. The hydrogen atoms of the alkyl group attached to the ring can be replaces by free radicals (such as H-O· and H-O-O·) more easily than hydrogen atom of the ring. Such free radicals may be generated from the decomposition of hydrogen peroxide by the presence of some cations. It is hypothesized that the formation of benzaldehyde will follow the mechanism similar to the halogenation of saturated hydrocarbon. The mechanism of the formation of benzaldehyde is showed in Figure 4.15. The active site in Figure 4.15 is possibly the cations of Co and Ti which act as acidic site having strength higher than any other catalysts.

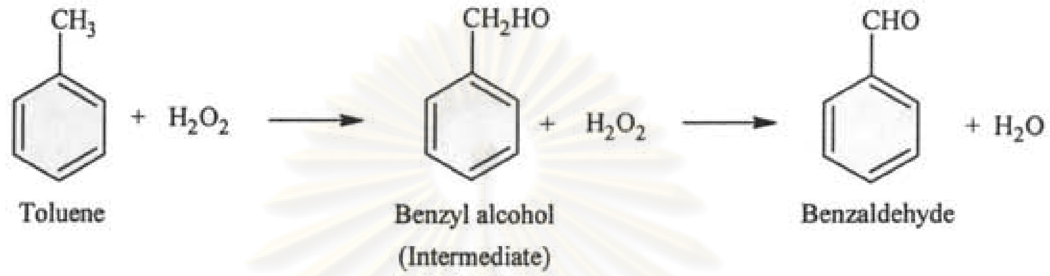


Figure 4.15 Mechanism of benzaldehyde formation.

4.5 Conclusions

From all of the experimental results and reasons described above, its can be concluded that Co-TS-1 has a potential to be used as a catalyst for the production of cresols via the reaction with hydrogen peroxide in a bubble reactor. The activity of the catalyst is related to the strength of the acid site of the catalyst. The weak of 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 RECOMMENDATIONS

In the present work, the hydroxylation of toluene in a bubble reactor over TS-1 and modified TS-1(Co-TS-1) catalysts using 3 and 7.5 wt% hydrogen peroxide concentration has been studied. The overall conclusions in the experiment are summarized in section 5.1. Section 5.2 is recommendation for further study.

5.1 Conclusions

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

2. The cresol product from toluene hydroxylation is believed that is performed by electrophilic aromatic substitution over TS-1 and Co-TS-1. The metal cation converts the H_2O_2 to more reactive electrophile that attacks the aromatic ring to from carbonium ion and abstraction photon to form the cresol product.

3. Co ion on catalyst enhance the formation of aromatic ring oxidation (cresol) Especially, Co-TS-1 gives a hundred percent selectivity of o-cresol product.

4. Co-TS-1(150), even though treated or no treatment HNO_3 have only cresol. Therefore Co-TS-1(150 N 1) has only o-cresol.

5. Lower concentration of H_2O_2 will increase cresol selectivity while higher concentration will increase benzadehyde selectivity.

5.2 Recommendations

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

1. Effects of toluene concentration and feed time should be further investigated.
2. A new reactor design which has better mixing between the gas bubble and H_2O_2 solution should be a subject for future study.

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APPENDICES

APPENDIX A

ZEOLITES

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

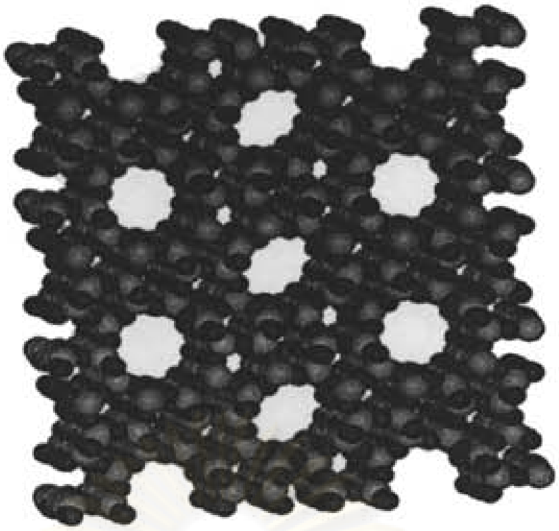


Figure A1 The micro porous molecular structure of a zeolite, ZSM-5. (en.wikipedia.org/wiki/Zeolite)

Shape selectivity

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

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

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

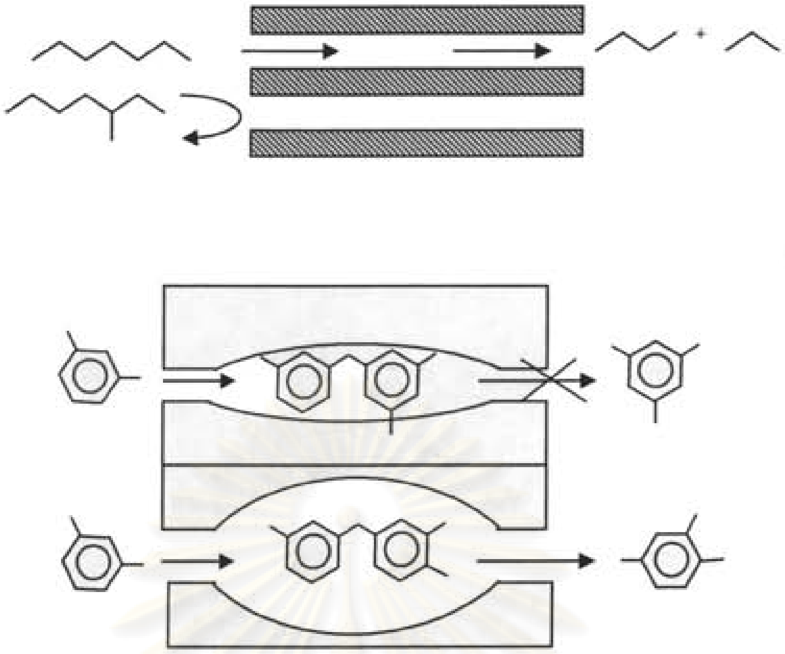


Figure A2 Diagram of shape selectivity on zeolite.

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

APPENDIX B

DATA OF EXPERIMENTS

Table B1 Data of experiments over Co-TS-1 catalyst at 7.5wt% of H_2O_2

		% conversion	Product (mole)			Benzaldehyde	รวม
			Benzaldehyde	o-cresol	p-cresol		
150	Co-TS-1 3D NO	0.0106	0	3.66252E-13	1.15096E-13	0	4.81348E-13
	Co-TS-1 3D treat	0.0299	1.65E-12	6.07175E-14	0	3.30718E-12	3.3679E-12
	Co-TS-1 1D NO	0.0089	1.45613E-13	9.28949E-14	1.63136E-13	2.91227E-13	5.47257E-13
	Co-TS-1 1D treat	0.0505	2.29219E-13	7.64063E-14	0	4.58438E-13	5.34844E-13
50	Co-TS-1 3D NO	0.0093	1.43236E-13	2.76942E-13	0	2.86473E-13	5.63414E-13
	Co-TS-1 3D treat	0.0192	8.0162E-13	6.70338E-14	0	1.60324E-12	1.67027E-12
	Co-TS-1 1D NO	0.0141	4.05632E-13	1.68535E-13	6.67394E-14	8.11265E-13	1.04654E-12
	Co-TS-1 1D treat	0.0877	3.77834E-12	1.94445E-13	0	7.55668E-12	7.75113E-12
300	Co-TS-1 3D NO	0.0054	1.11315E-13	7.46404E-14	5.92233E-14	2.22631E-13	3.56495E-13
	Co-TS-1 3D treat	0.0377	1.39994E-12	1.28657E-13	1.82085E-13	2.79989E-12	3.11063E-12
	Co-TS-1 1D NO	0.0075	2.45315E-13	9.25478E-14	0	4.9063E-13	5.83178E-13
	Co-TS-1 1D treat	0.0178	7.52041E-13	5.66878E-14	0	1.50408E-12	1.56077E-12

Table B2 Data of experiments over Co-TS-1 catalyst at 3wt% of H_2O_2

		% conversion	Product(mole)			Benzaldehyde	รวม
			Benzaldehyde	o-cresol	p-cresol		
150	Co-TS-1 3D NO	0.0398	0	2.05108E-13	8.77634E-14	0	2.05E-13
	Co-TS-1 3D treat	0.0270	0	3.95637E-13	9.32949E-14	0	4.88932E-13
	Co-TS-1 1D NO	0.0083	0	1.51228E-13	0	0	1.51228E-13
	Co-TS-1 1D treat	0.0913	0	1.04936E-12	6.06156E-13	0	1.65551E-12
50	Co-TS-1 3D NO	0.0319	1.3332E-13	3.15963E-13	1.29472E-13	2.66641E-13	7.12076E-13
	Co-TS-1 3D treat	0.0691	1.18601E-12	6.64527E-14	0	2.37201E-12	2.43846E-12
	Co-TS-1 1D NO	0.0422	6.96418E-13	6.83242E-14	0	1.39284E-12	1.46116E-12
	Co-TS-1 1D treat	0.0467	7.10273E-13	1.36173E-13	0	1.42055E-12	1.55672E-12
300	Co-TS-1 3D NO	0.0048	0	6.22796E-14	2.47217E-14	0	8.70013E-14
	Co-TS-1 3D treat	0.0186	2.10949E-13	9.87508E-14	2.83439E-14	4.21898E-13	5.48993E-13
	Co-TS-1 1D NO	0.0230	1.07716E-13	3.59053E-14	2.72391E-13	2.15432E-13	5.23728E-13
	Co-TS-1 1D treat	0.0394	6.73054E-13	4.04104E-14	0	1.34611E-12	1.38652E-12

Table B3 Data of experiments over TS-1 and Co-TS-1 catalyst

Co-TS-1	Day	Ratio Si/Co	wt% H_2O_2	% conversion H_2O_2	% Selectivity		
					Benzaldehyde	*o*-cresol	*p*-cresol
Treated	3	50	7.5	0.0192	85.67	14.33	0
			3	0.0691	89.93	10.07	0
		150	7.5	0.0299	62.42	23.04	14.53
			3	0.027	0	80.91	19.09
		300	7.5	0.0377	69.25	12.72	18.01
			3	0.0186	45.35	42.46	12.18
	1	50	7.5	0.0877	90.67	9.33	0
			3	0.0467	66.17	33.83	0
		150	7.5	0.0505	60	40	0
			3	0.1896	0	63.38	36.62
		300	7.5	0.0178	86.89	13.10	0
			3	0.0394	89.27	10.72	0
No treatment	3	50	7.5	0.0093	85.67	14.32	0
			3	0.0192	13.02	61.7	25.28
		150	7.5	0.0106	0	76.088	23.92
			3	0.0913	0	63.385	36.614
		300	7.5	0.0054	29.36	39.38	31.24
			3	0.0048	0	71.58	28.42
	1	50	7.5	0.0141	46.29	38.47	15.23
			3	0.0422	83.59	16.41	0
		150	7.5	0.0089	22.14	28.24	49.60
			3	0.0083	0	100	0
		300	7.5	0.0075	56.99	43.01	0
			3	0.023	14.87	9.91	75.21

APPENDIX C

CALIBRATION CURVES

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

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

Mole of reagent in y-axis and area reported by gas chromatography in x-axis are exhibited in the curves. The calibration curves of benzaldehyde, *o*-cresol, *p*-cresol, toluene are illustrated in Figure C1-C3, respectively.

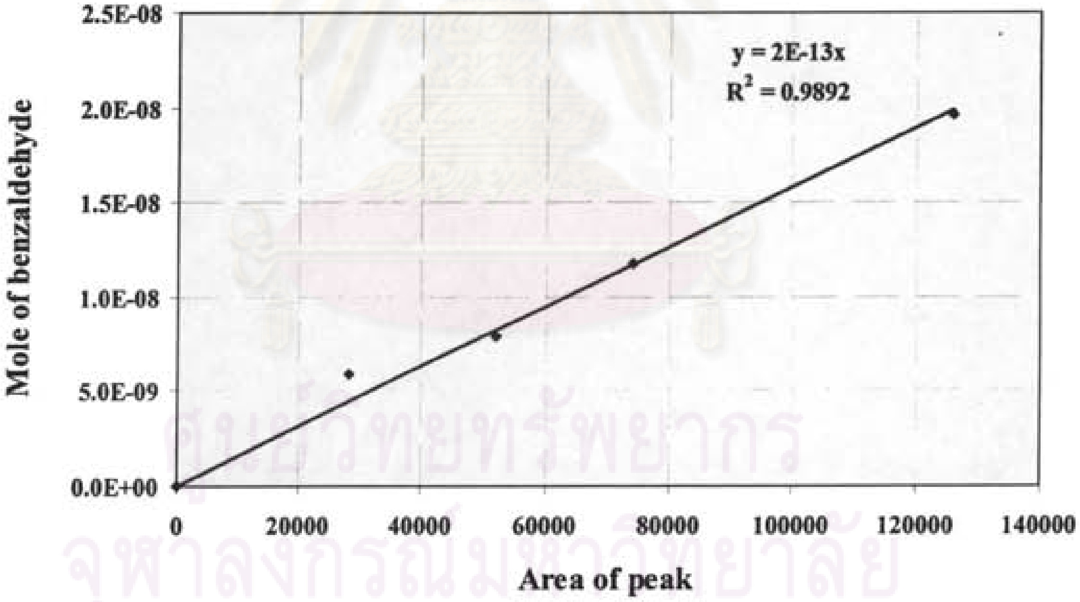


Figure C1 The calibration curve of benzaldehyde.

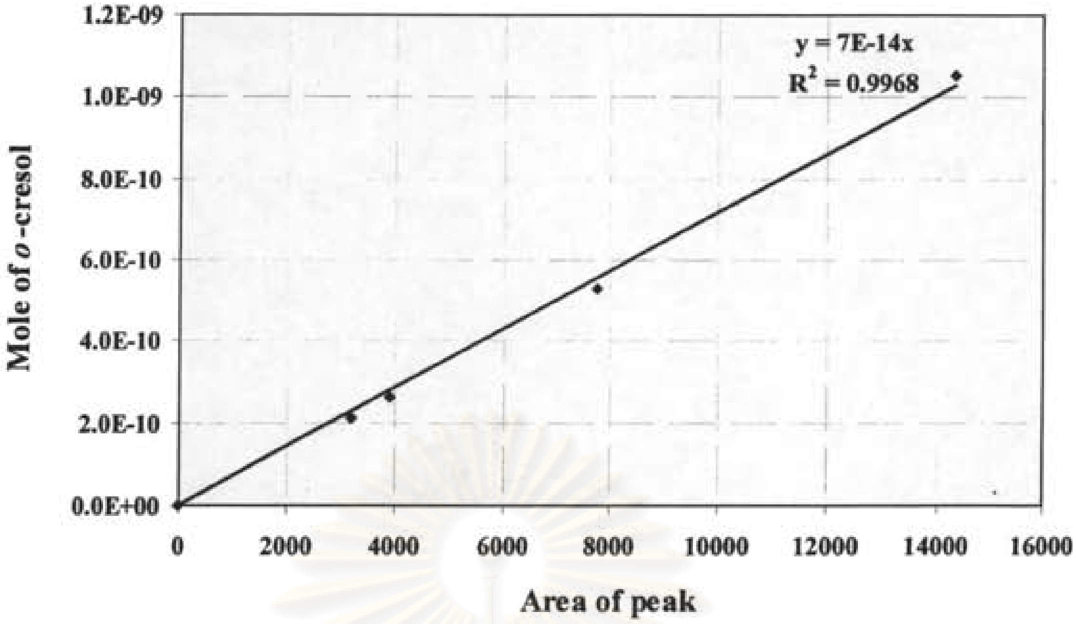


Figure C2 The calibration curve of *o*-cresol.

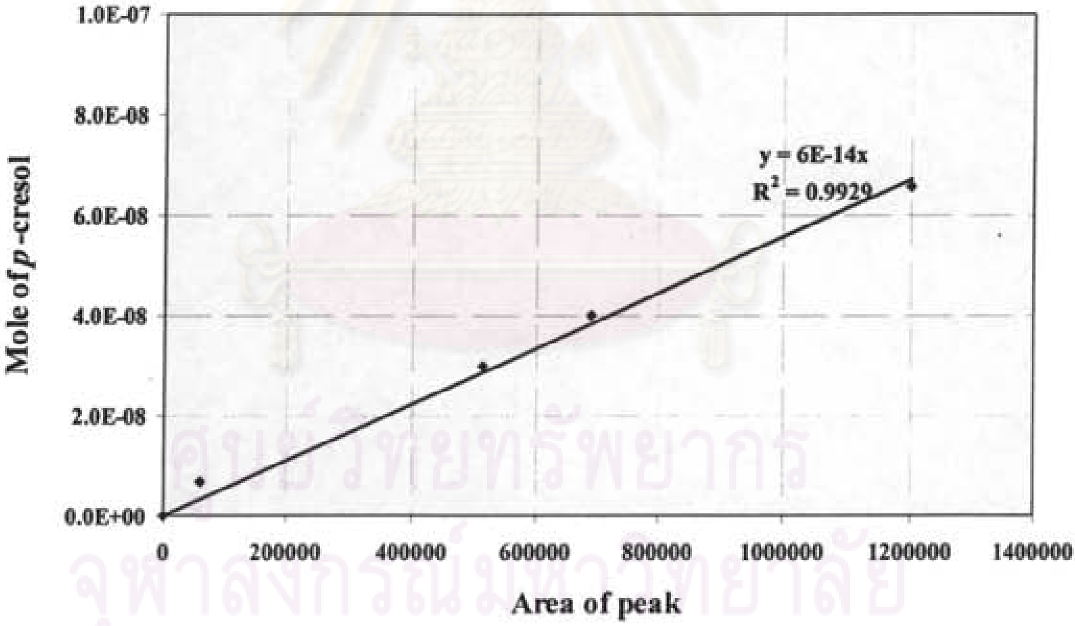


Figure C3 The calibration curve of *p*-cresol.

APPENDIX D

CALCULATION OF CONVERSION

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

Activity of the catalyst performed in term conversion. The conversion is defined as overall mole of products with respect to overall mole of reactant feeding.

Example, in case of Hydrogen peroxide hydroxylation

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

Where overall mole of *o*-cresol can be measured as follows:

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

Where mole of *o*-cresol can be measured employing the calibration curve of *o*-cresol in Figure B2, Appendix B.,i.e.,

$$\text{Mole of } o\text{-cresol} = ((\text{area of } o\text{-cresol peak from integrator plot on GC-9A}) \text{ X } (\text{slope of calibration cave of o-cresol})) \qquad \text{(D3)}$$

$$\text{Mole of all products} = (\text{mole of benzaldehyde} + \text{mole of o-cresol} + \text{mole of p-cresol}) \qquad \text{(D4)}$$

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

$$\text{\% Selectivity of } o\text{-cresol} = \frac{\text{Mole of } o\text{-cresol}}{\text{Mole of all products}} \qquad \text{(D5)}$$

Where overall mole of benzene can be measured as follows:

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

$$\text{Overall mole of toluene} = \frac{\text{Volume of toluene feeding} \times 0.903}{92.14} \qquad \text{(D6)}$$

Where overall mole of hydrogen peroxide can be measured as follows:

$$\text{Overall mole of } H_2O_2 = \frac{\text{Volume of toluene feeding} \times \text{Density of } H_2O_2}{\text{Molecular weight of } H_2O_2} \qquad \text{(D7)}$$

APPENDIX E

CALCULATION FOR CATALYST PREPARATION

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

Molecular Weight of Si	=	28.0855
Molecular Weight of SiO_2	=	60.0843
Weight percent of SiO_2 in sodium Silicate	=	28.5

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

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

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

$$= 0.3273$$

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 $= 0.3273/50$

$= 6.546 \times 10^{-3}$ 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/Ti 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 F

DATA OF CALCULATION OF ACID SITE

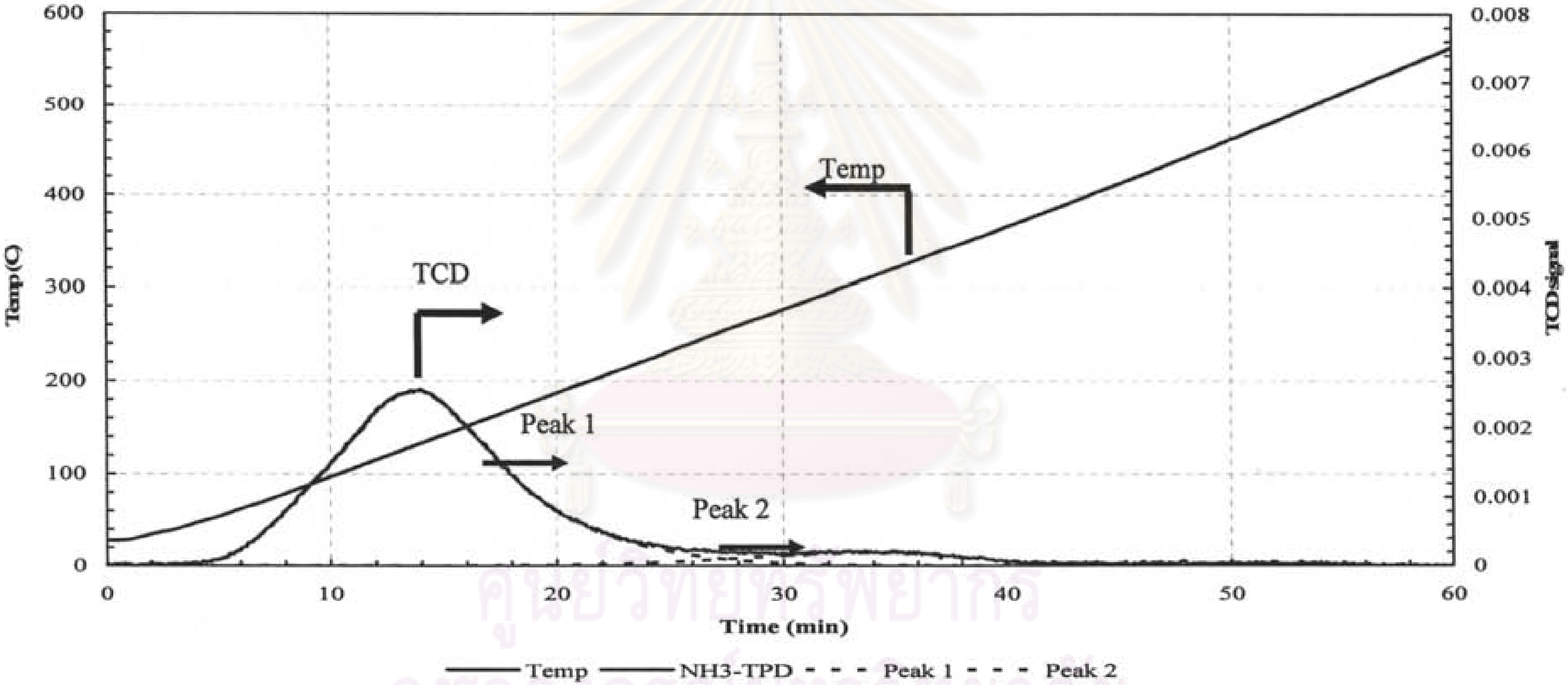


Figure F1 TCD signal and temperature versus time of TS-1(3 day) from Micromeritrics Chemisorb 2750.

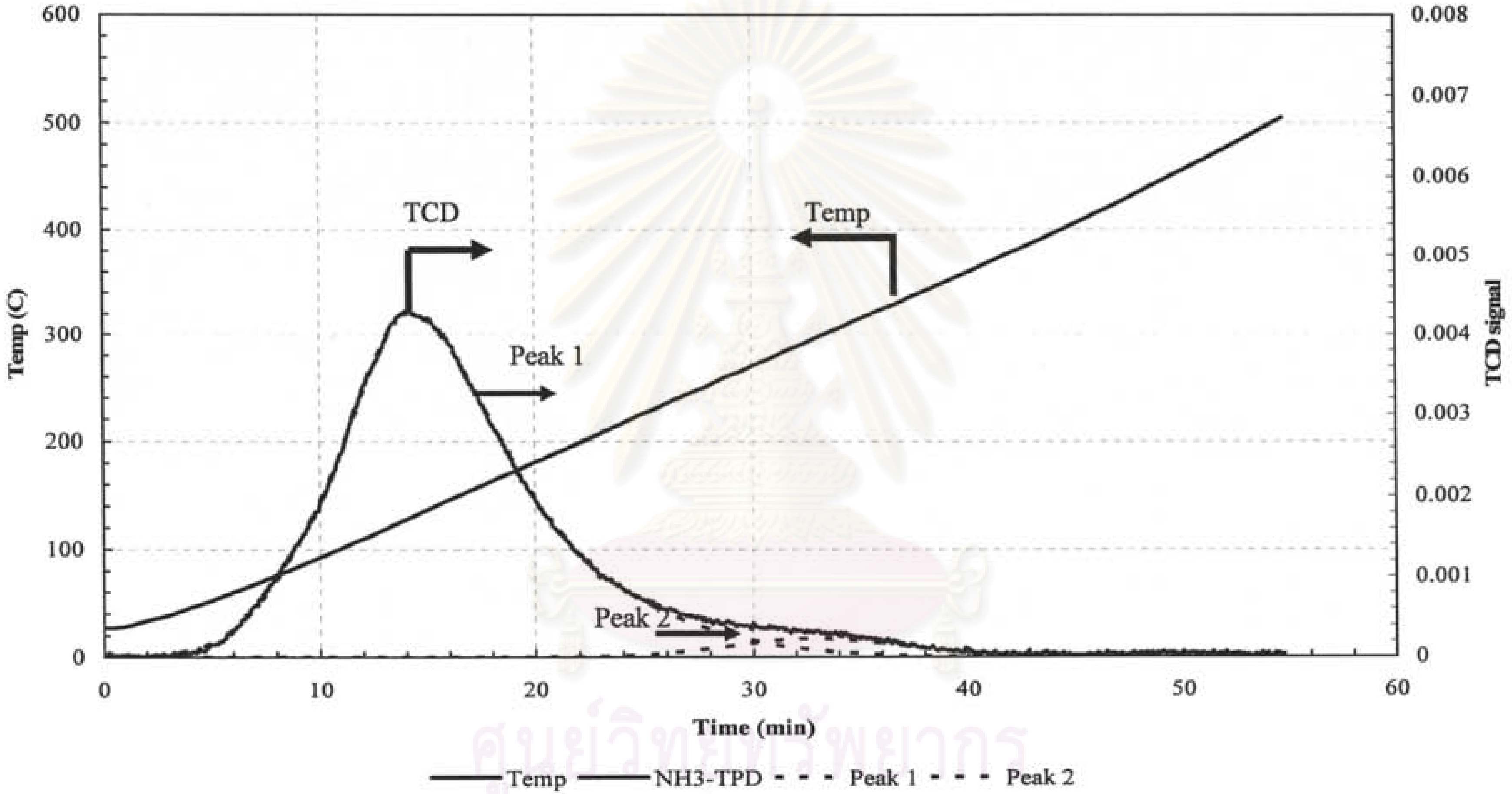


Figure F2 TCD signal and temperature versus time of TS-1(1 day) from Micromeritrics Chemisorb 2750.

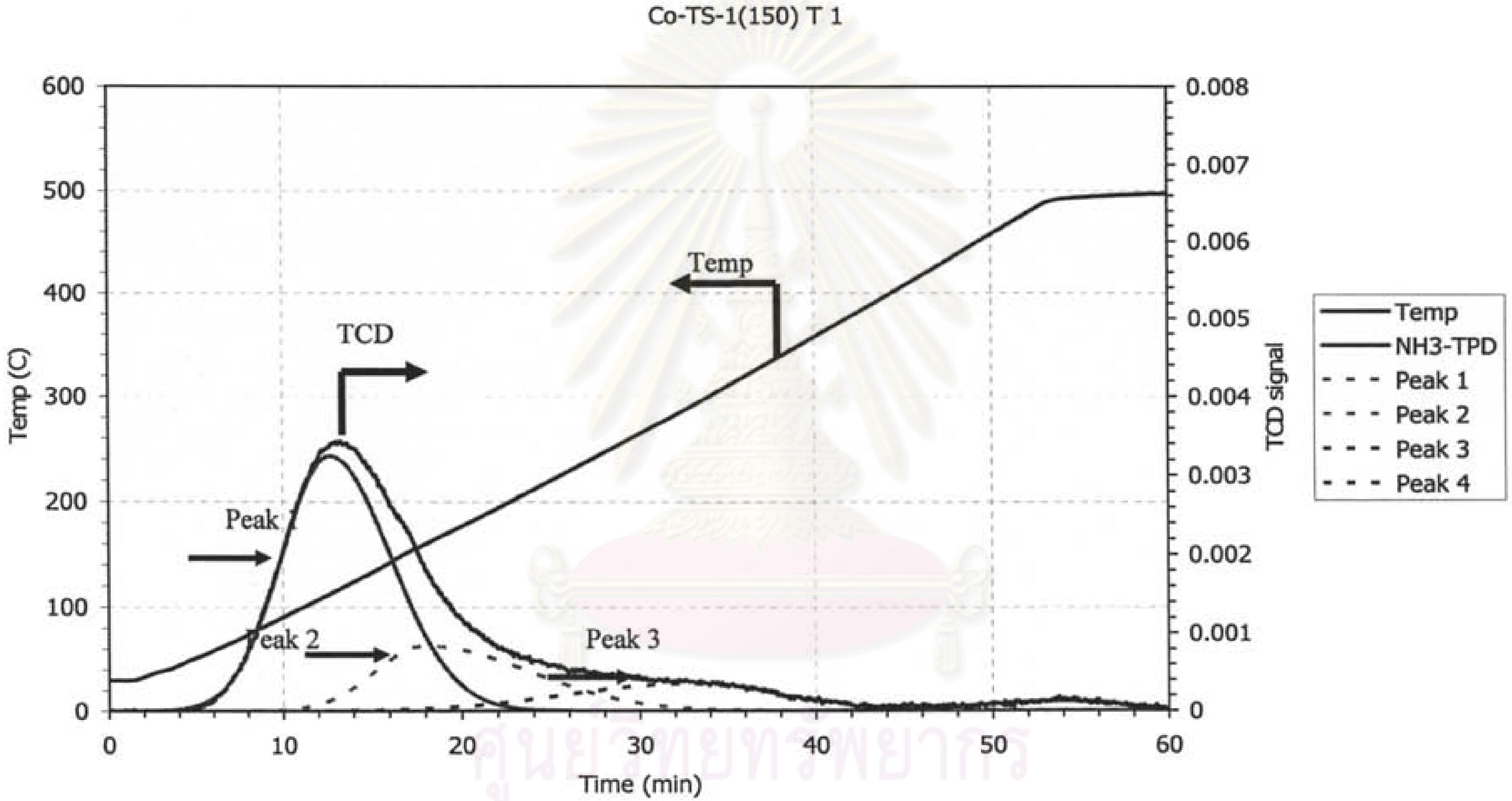


Figure F3 TCD signal and temperature versus time of Co-TS-1 (150 T 1)from Micromeritrics Chemisorb 2750.

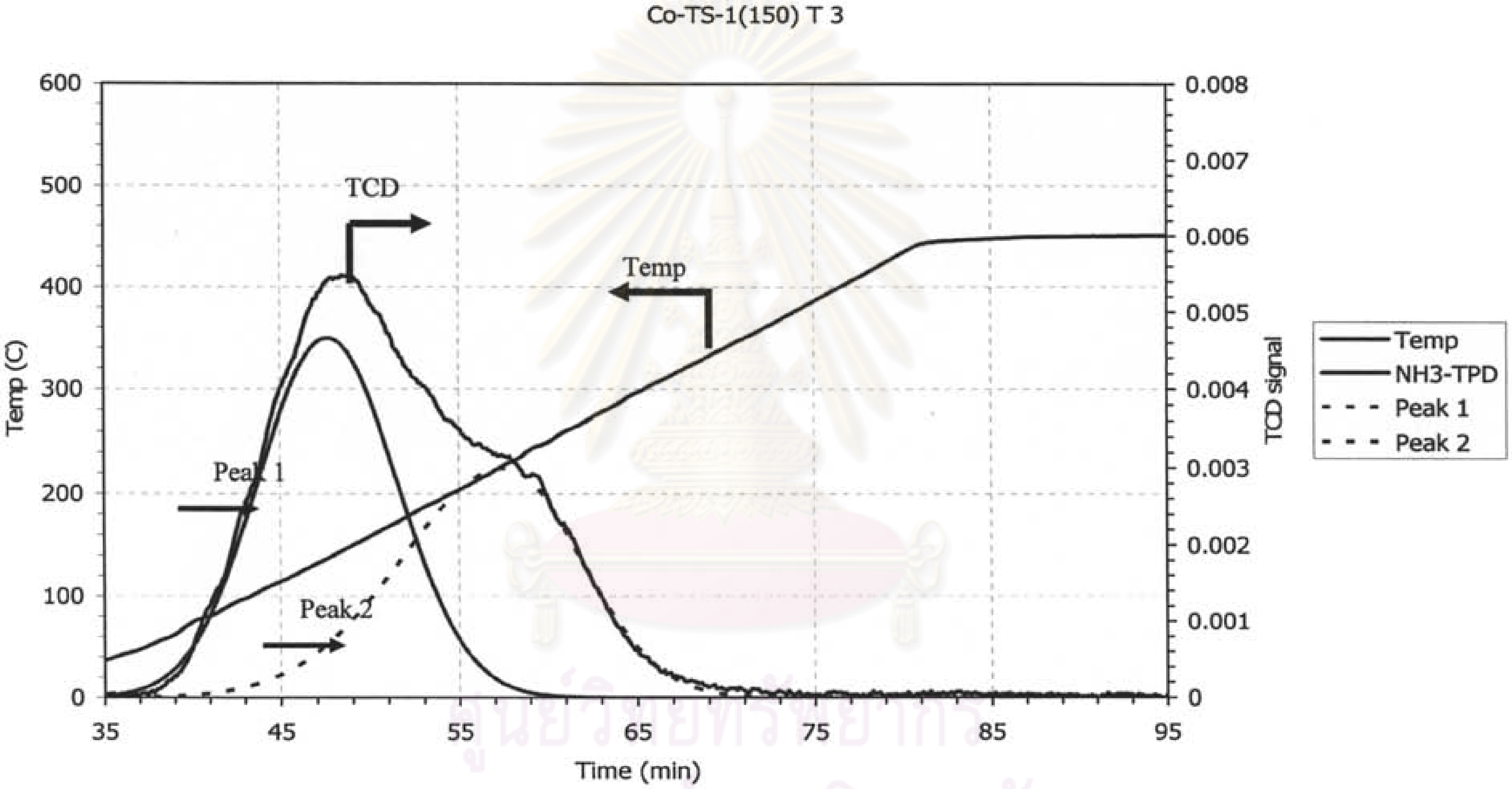


Figure F4 TCD signal and temperature versus time of Co-TS-1 (150 T 3)from Micromeritrics Chemisorb 2750.

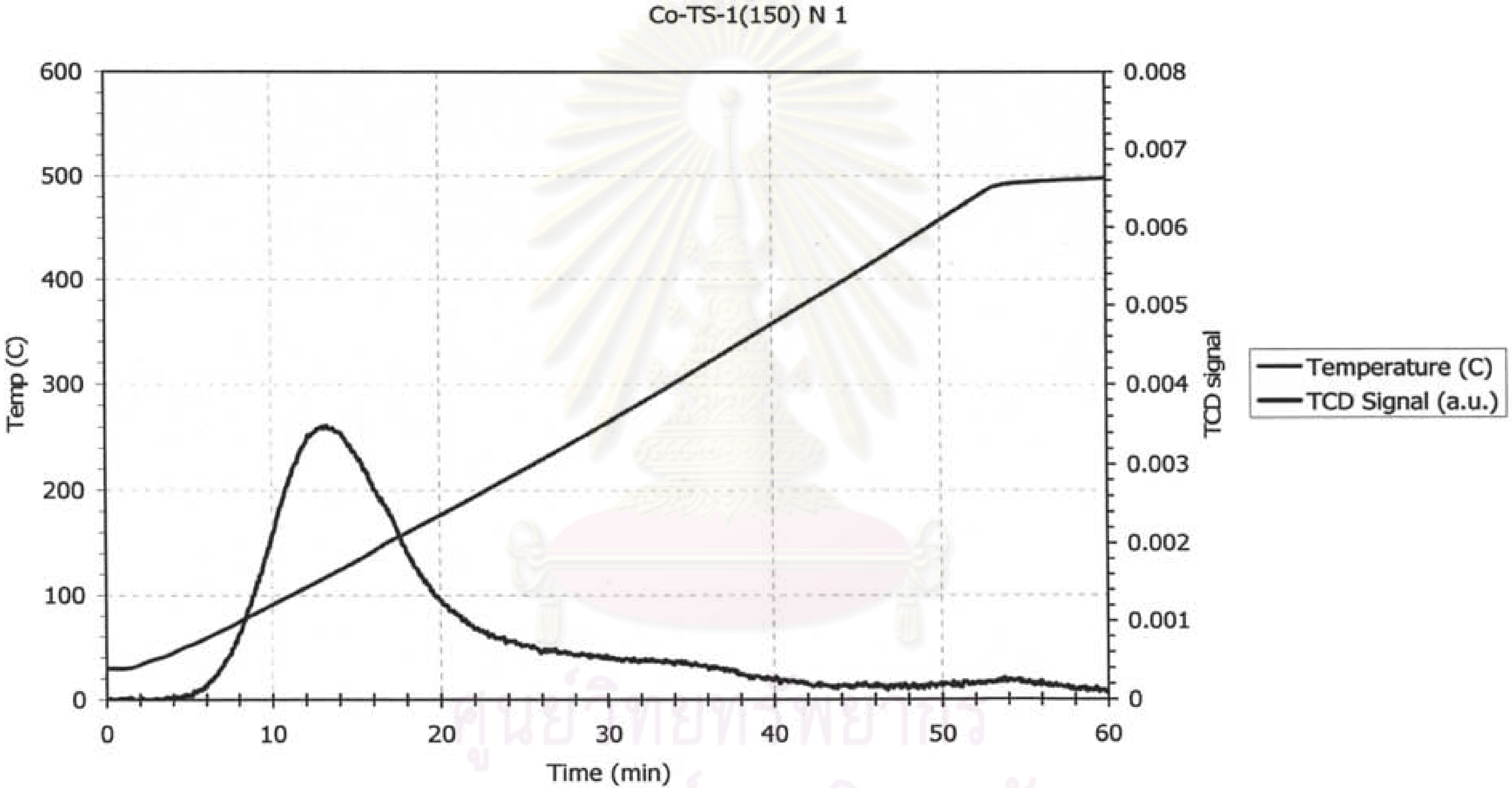


Figure F5 TCD signal and temperature versus time of Co-TS-1(150 N 1) from Micromeritrics Chemisorb 2750.

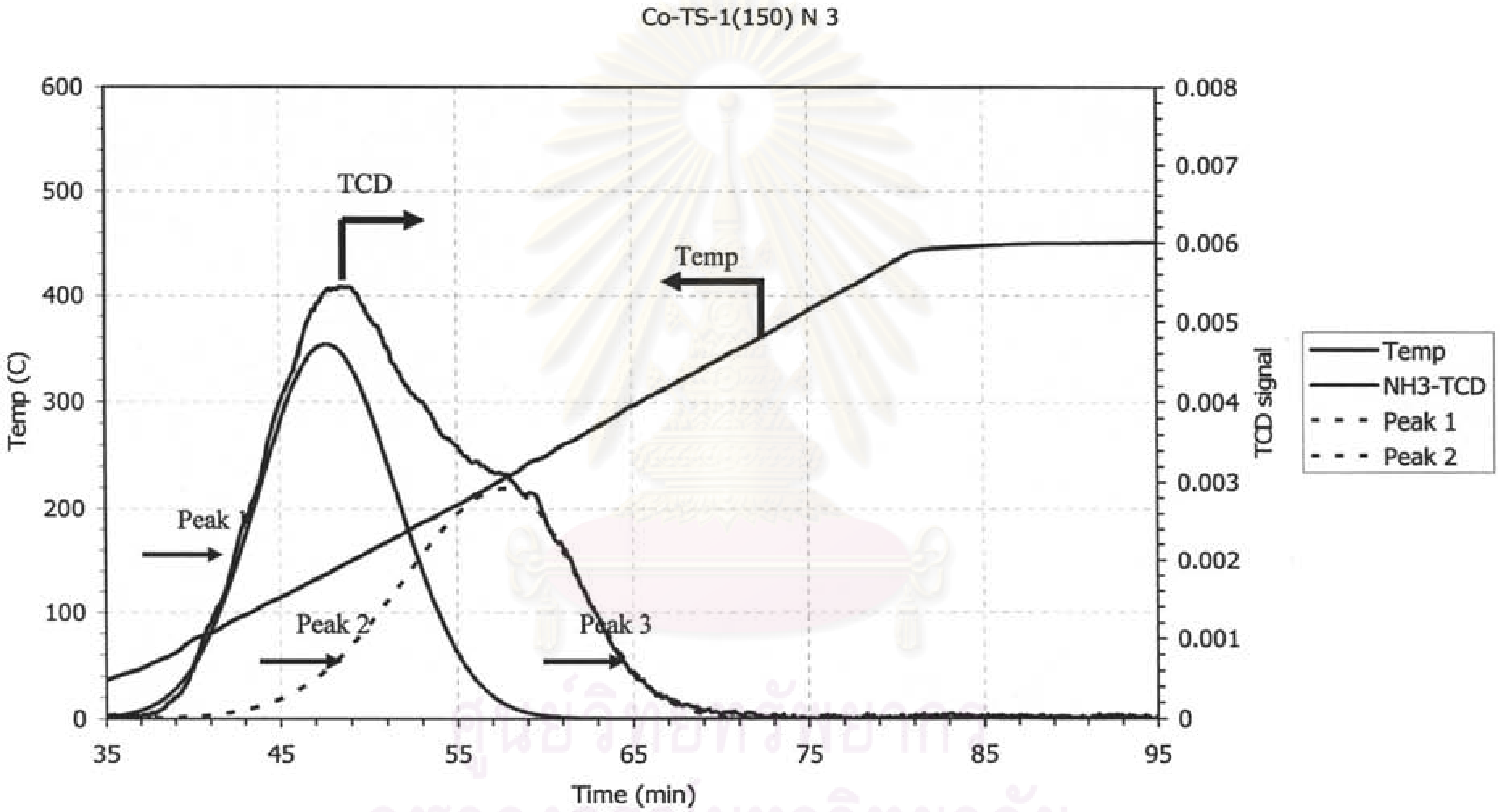


Figure F6 TCD signal and temperature versus time of Co-TS-1(150 N 3) from Micromeritrics Chemisorb 2750.

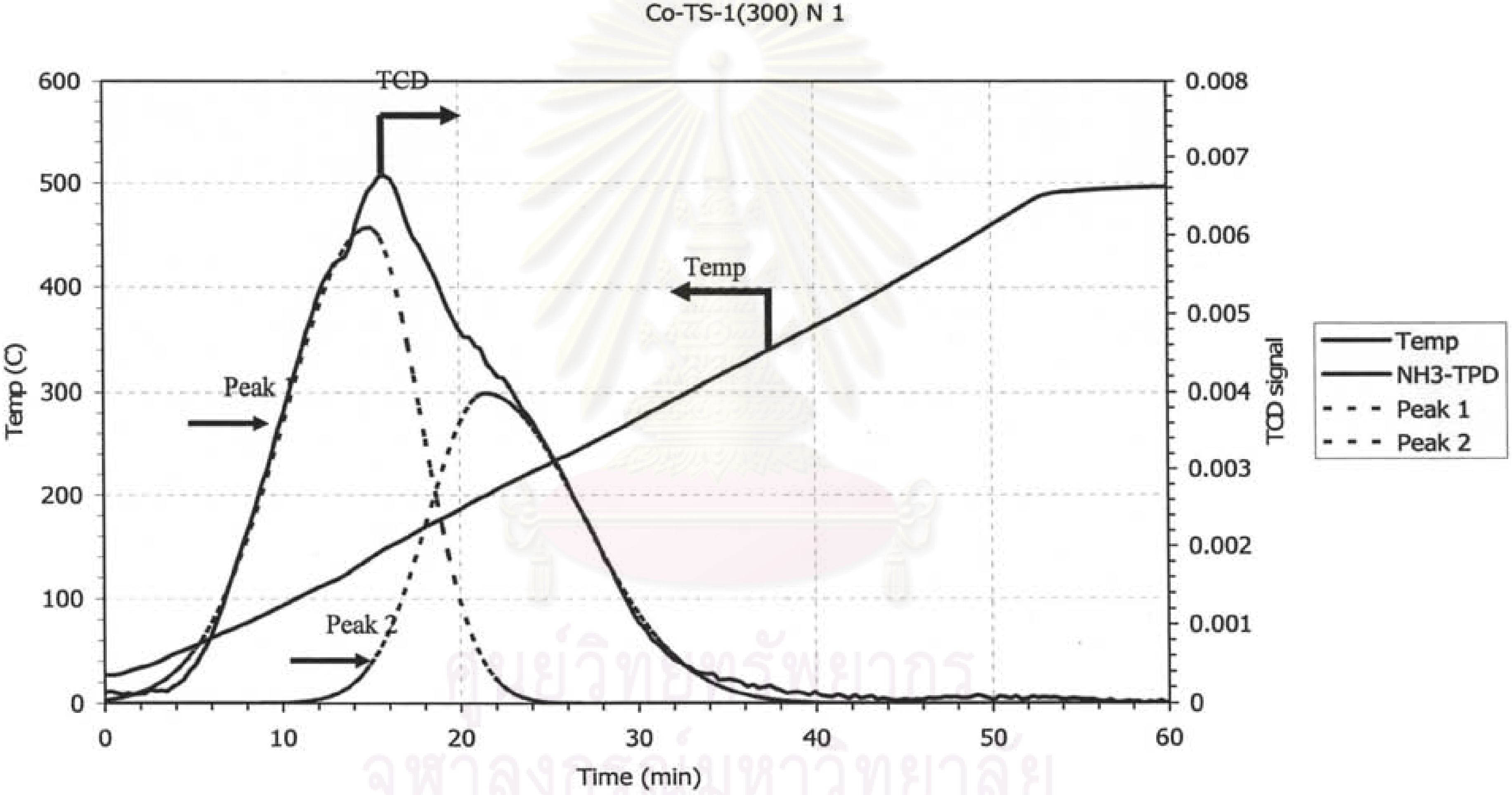
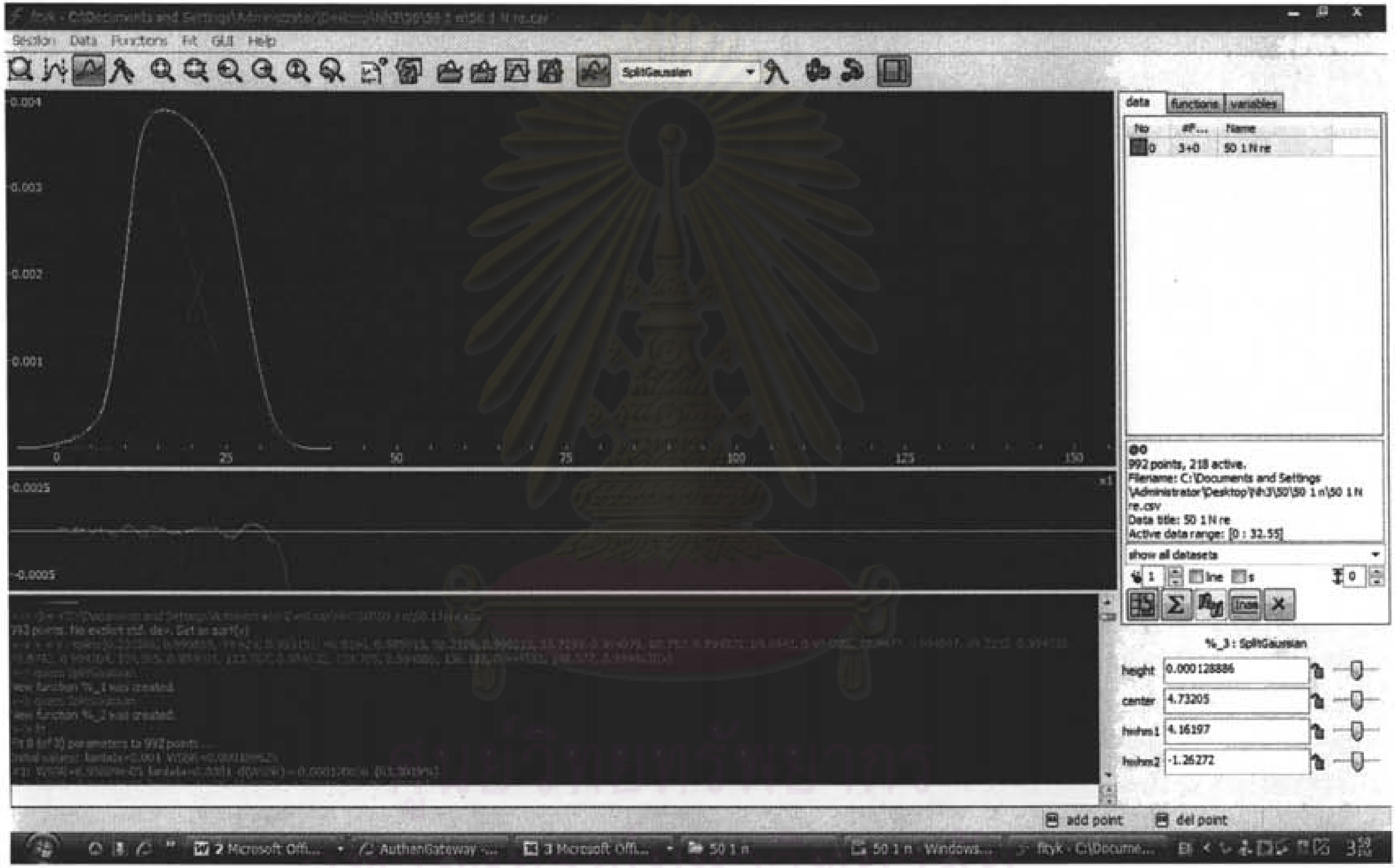


Figure F7 TCD signal and temperature versus time of Co-TS-1(300 N 1) from Micromeritics Chemisorb 2750.



```
992 points. No explicit std. dev. Set as sqrt(y)
New function %_1 was created.
New function %_2 was created.
```

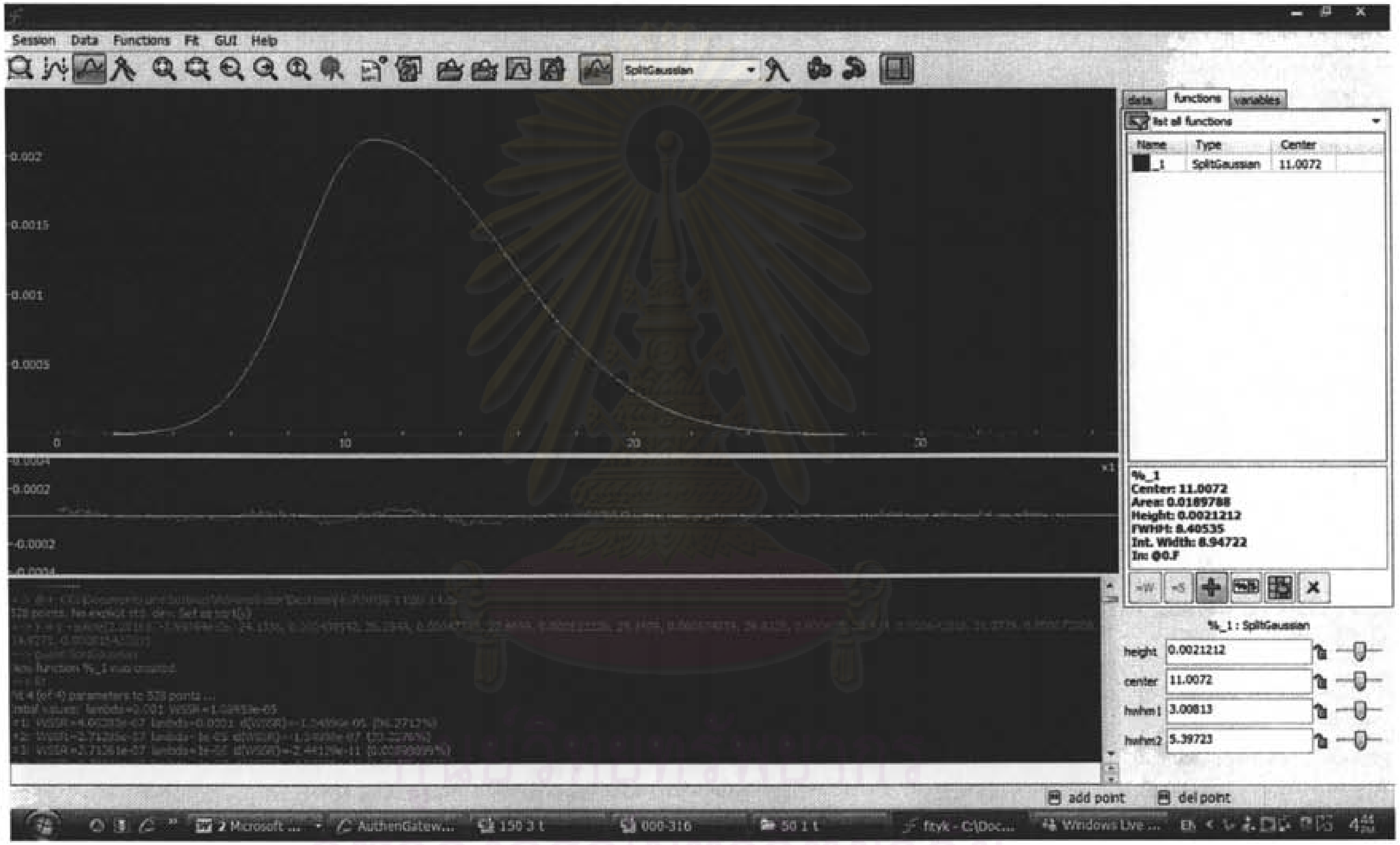
@0
992 points, 218 active.
Filename: C:\Documents and Settings\Administrator\Desktop\Nh3\50\50 1 n\50 1 N re.csv
Data title: 50 1 N re
Active data range: [0 : 32.55]

show all datasets

%_3 : SplitGaussian

height 0.000128886
center 4.73205
hwhm1 4.16197
hwhm2 -1.26272

Figure F8 Curve fitting of acid site ratio of CoTS-1(50 N 1) from fitting program.

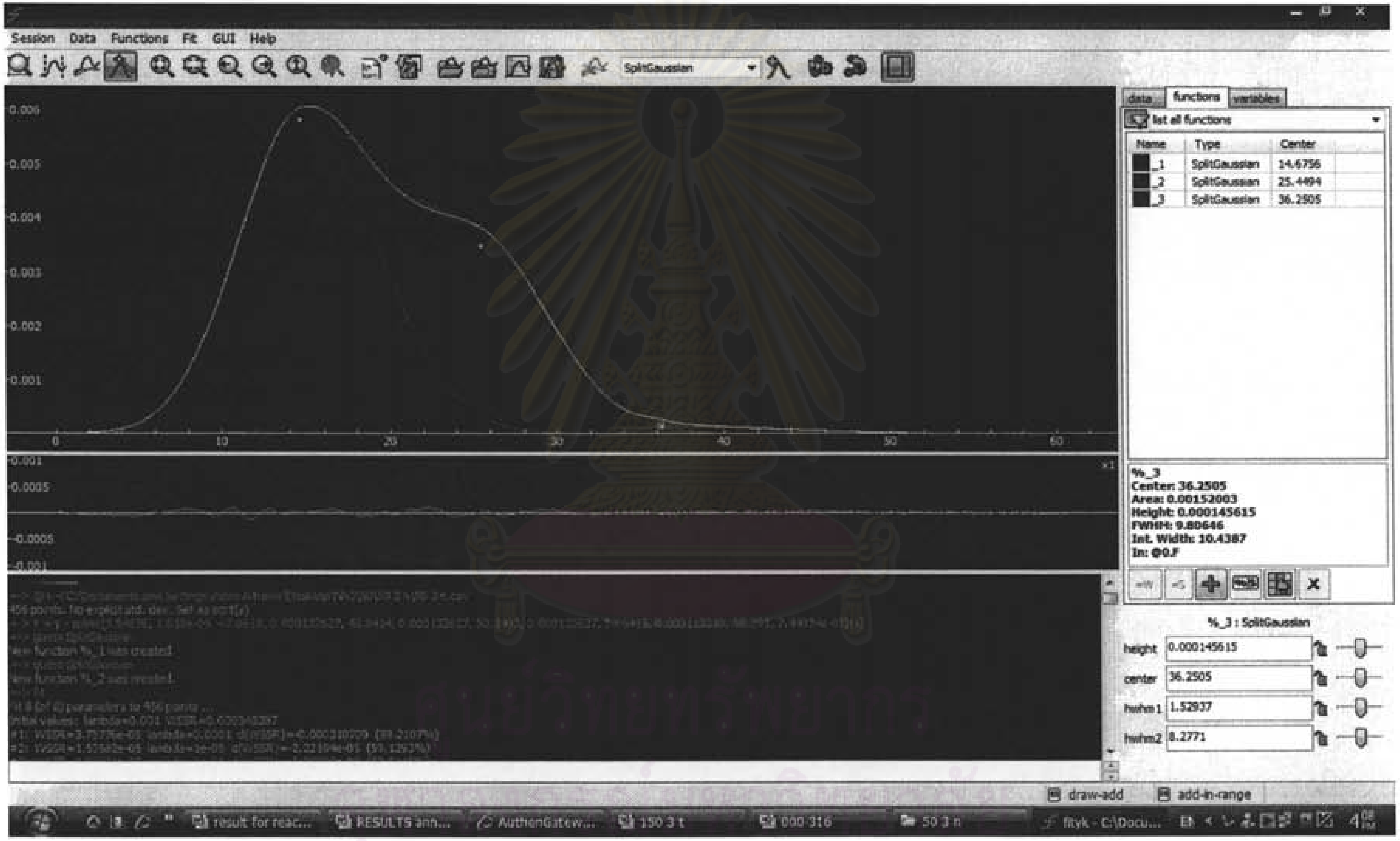


%_1
Center: 11.0072
Area: 0.0189788
Height: 0.0021212
FWHM: 8.40535
Int. Width: 8.94722
In: @0.F

%_1 : SplitGaussian

height 0.0021212
center 11.0072
hwhm1 3.00813
hwhm2 5.39723

Figure F9 Curve fitting of acid site ratio of CoTS-1(50 T 1) from fitting program.



Name	Type	Center
_1	SplitGaussian	14.6756
_2	SplitGaussian	25.4494
_3	SplitGaussian	36.2505

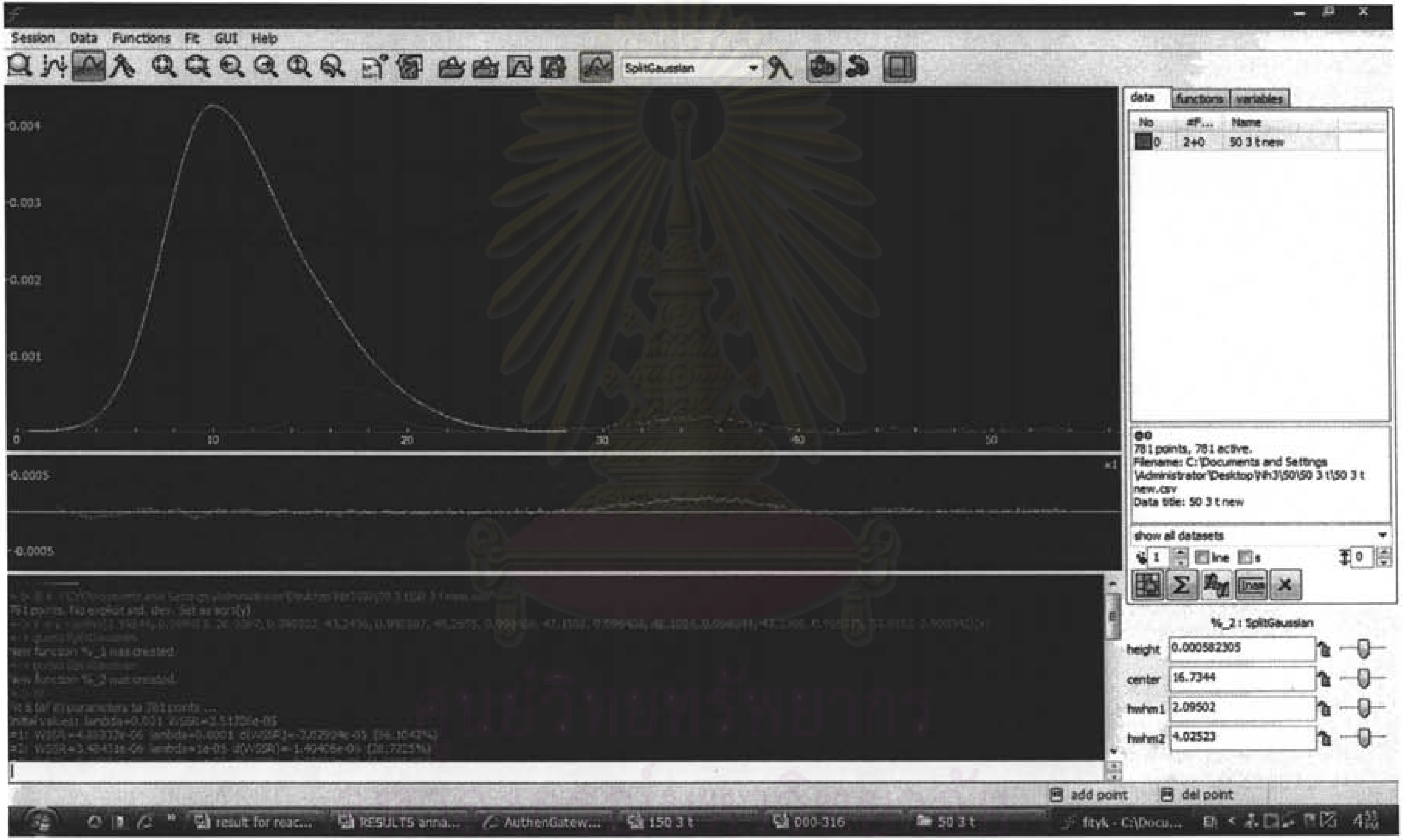
%_3
Center: 36.2505
Area: 0.00152003
Height: 0.000145615
FWHM: 9.80646
Int. Width: 10.4387
In: @0.F

%_3 : SplitGaussian

height 0.000145615
center 36.2505
hwhm1 1.52937
hwhm2 8.2771

```
[illegible]
456 points. [illegible]
[illegible]
[illegible]
New function %_1 was created.
[illegible]
New function %_2 was created.
[illegible]
Fit 8 (of 8) parameters to 456 points ...
Initial values: lambda=0.001 WSSR=[illegible]
#1: WSSR=[illegible] lambda=0.0001 d(WSSR)=[illegible]
#2: WSSR=[illegible] lambda=1e-05 d(WSSR)=[illegible]
```

Figure F10 Curve fitting of acid site ratio of CoTS-1(50 N 3) from fitting program.



```
781 points. No explicit std. dev. Set as sqrt(y)
New function %_1 was created.
New function %_2 was created.
Fit 8 (of 8) parameters to 781 points ...
Initial values: lambda=0.001 WSSR=3.51726e-05
#1: WSSR=4.88332e-06 lambda=0.0001 d(WSSR)=-3.02924e-05 (86.1042%)
#2: WSSR=3.48431e-06 lambda=1e-05 d(WSSR)=-1.40406e-06 (28.7223%)
```

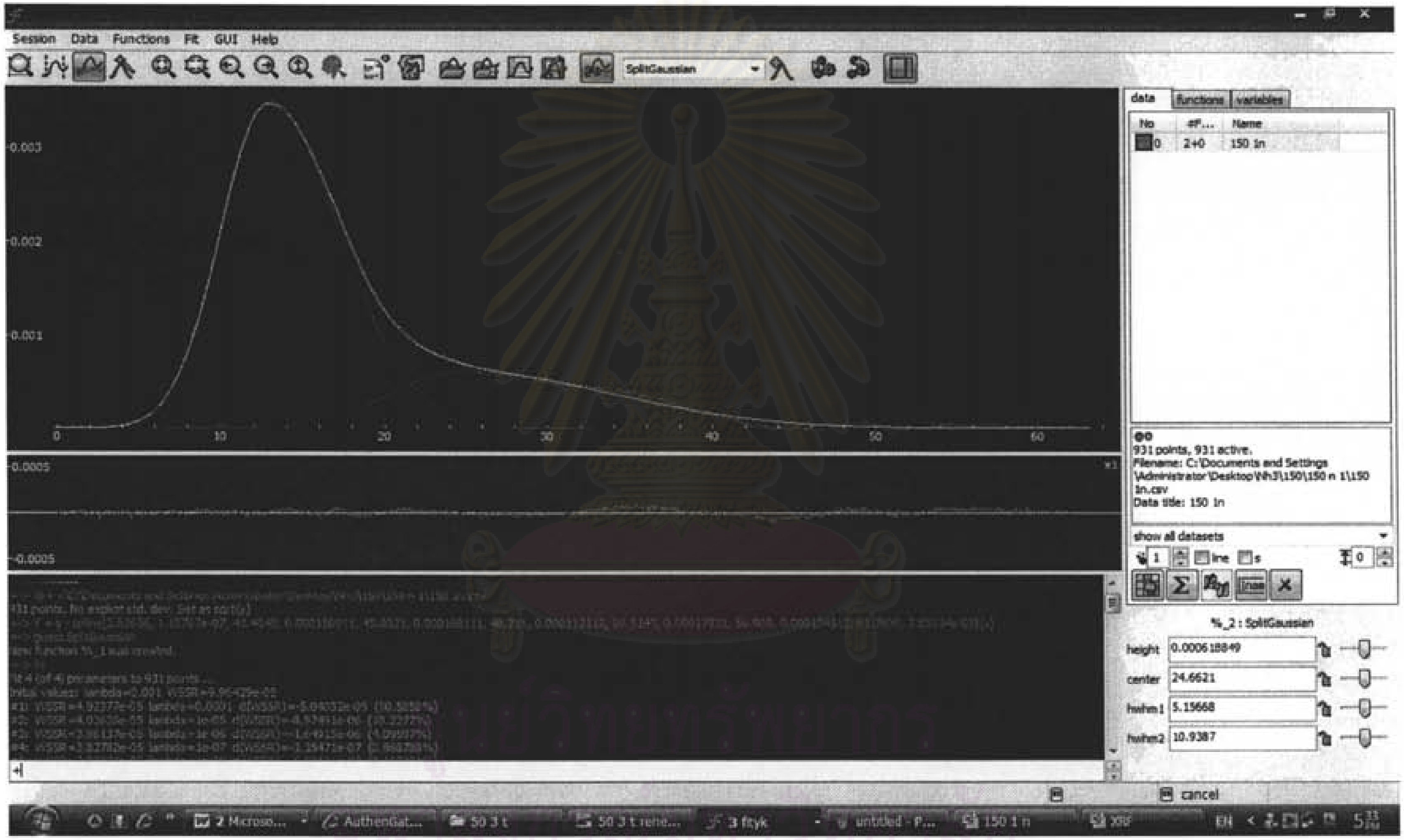
No	#F...	Name
0	2+0	50 3 t new

@0
781 points, 781 active.
Filename: C:\Documents and Settings\Administrator\Desktop\Nh3\50\50 3 t\50 3 t new.csv
Data title: 50 3 t new

%_2 : SplitGaussian

height 0.000582305
center 16.7344
hwhm1 2.09502
hwhm2 4.02523

Figure F11 Curve fitting of acid site ratio of CoTS-1(50 T 3) from fitting program.



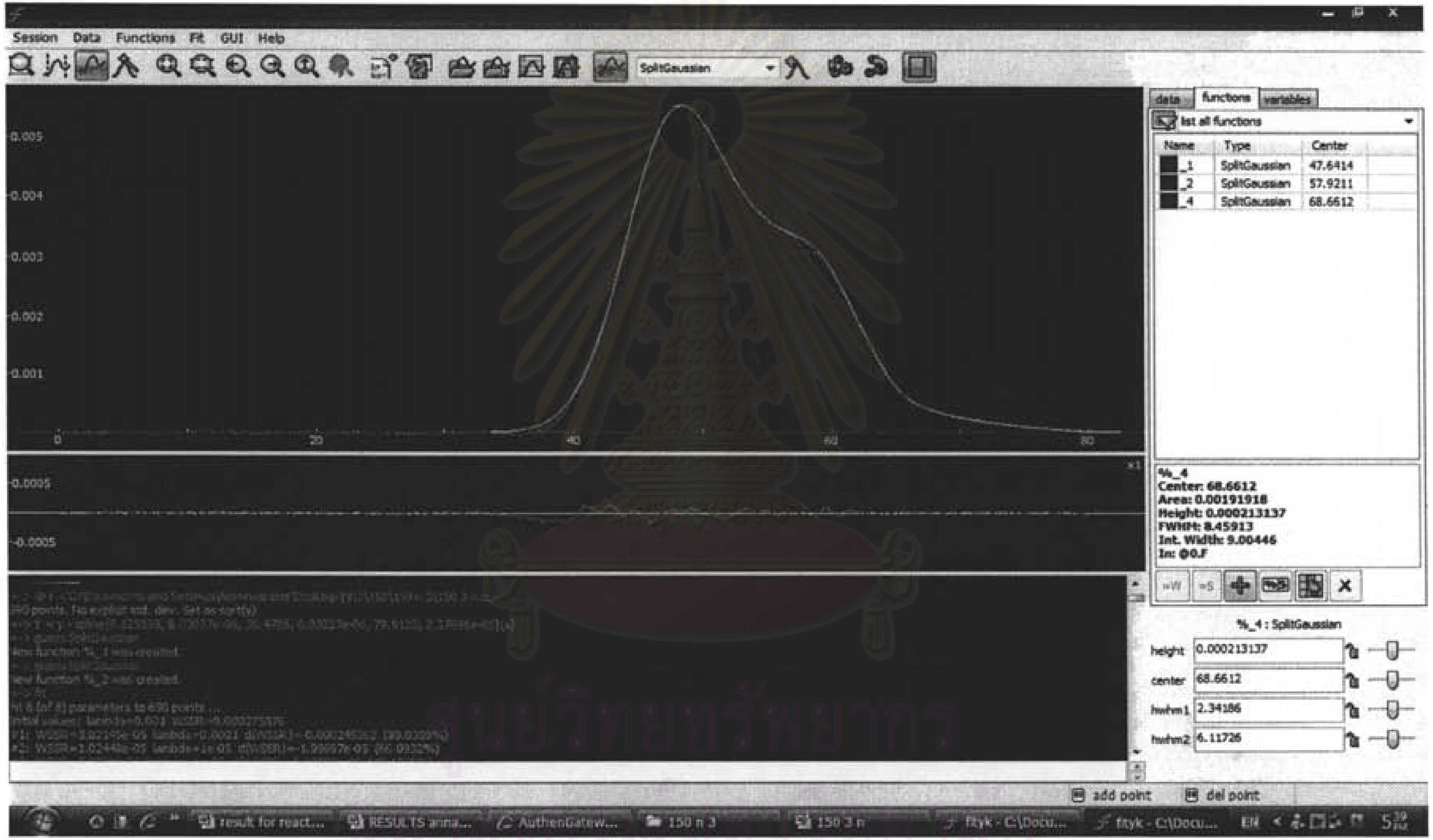
No	#F...	Name
0	2+0	150 1n

@0
931 points, 931 active.
Filename: C:\Documents and Settings\Administrator\Desktop\Nh3\150\150 n 1\150 1n.csv
Data title: 150 1n

%_2 : SplitGaussian

height 0.000618849
center 24.6621
hwhm1 5.15668
hwhm2 10.9387

Figure F12 Curve fitting of acid site ratio of CoTS-1(150 N 1) from fitting program.



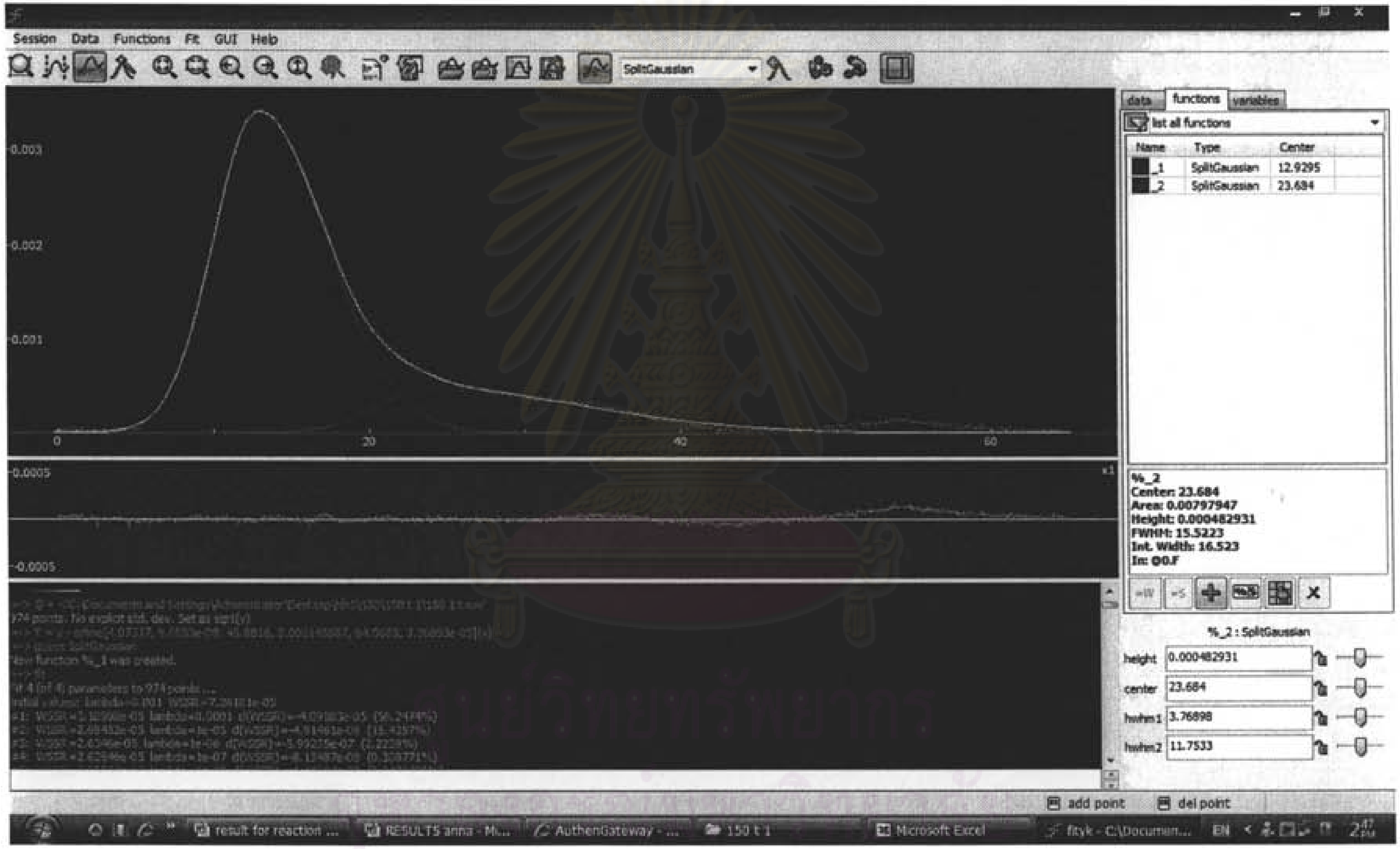
Name	Type	Center
_1	SplitGaussian	47.6414
_2	SplitGaussian	57.9211
_4	SplitGaussian	68.6612

%_4
Center: 68.6612
Area: 0.00191918
Height: 0.000213137
FWHM: 8.45913
Int. Width: 9.00446
In: @0.F

%_4 : SplitGaussian

height 0.000213137
center 68.6612
hwhm1 2.34186
hwhm2 6.11726

Figure F13 Curve fitting of acid site ratio of CoTS-1(150 N 3) from fitting program.



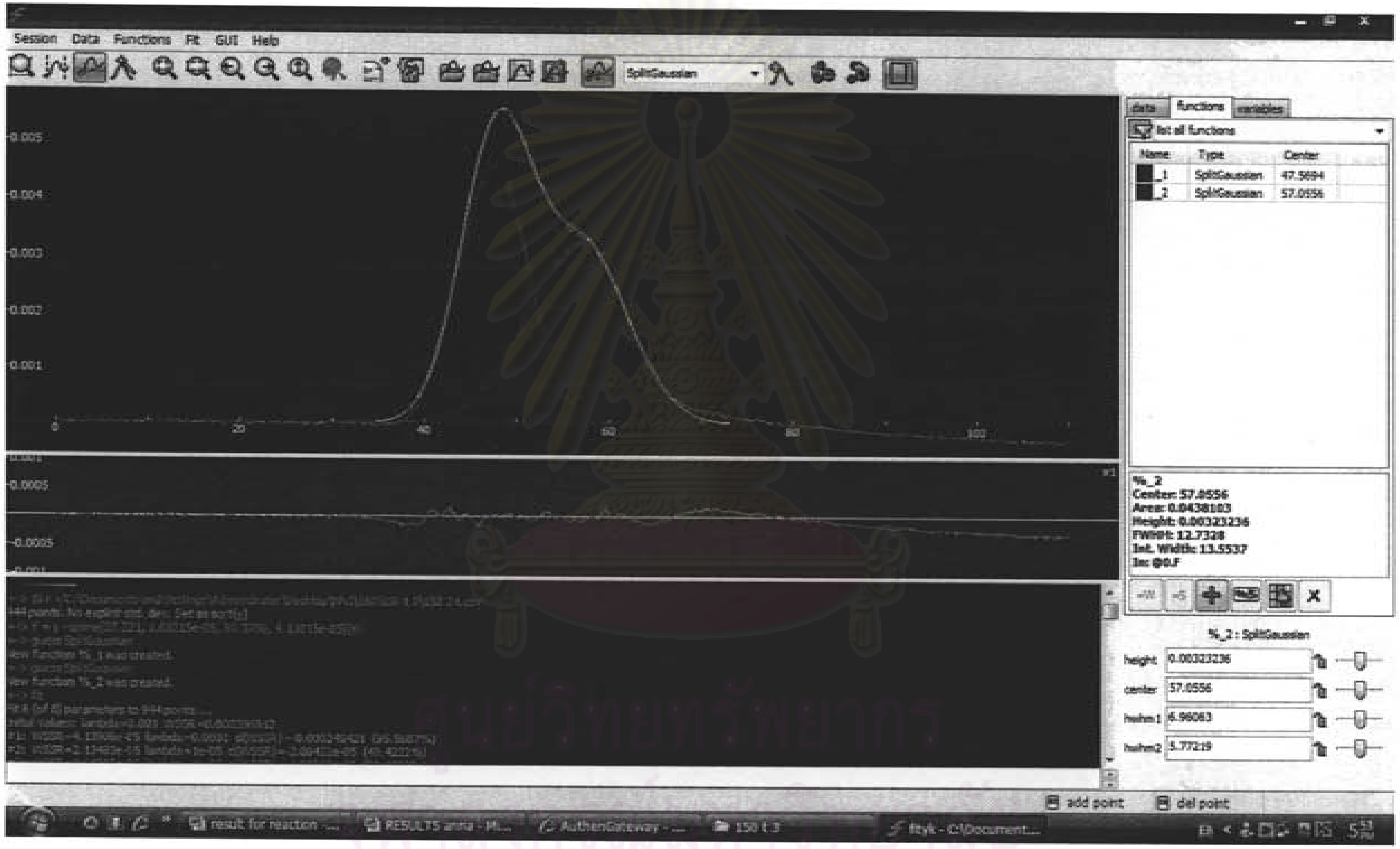
Name	Type	Center
%_1	SplitGaussian	12.9295
%_2	SplitGaussian	23.684

%_2
Center: 23.684
Area: 0.00797947
Height: 0.000482931
FWHM: 15.5223
Int. Width: 16.523
In: @0.F

%_2 : SplitGaussian

height 0.000482931
center 23.684
hwhm1 3.76898
hwhm2 11.7533

Figure F14 Curve fitting of acid site ratio of CoTS-1(150 T 1) from fitting program.



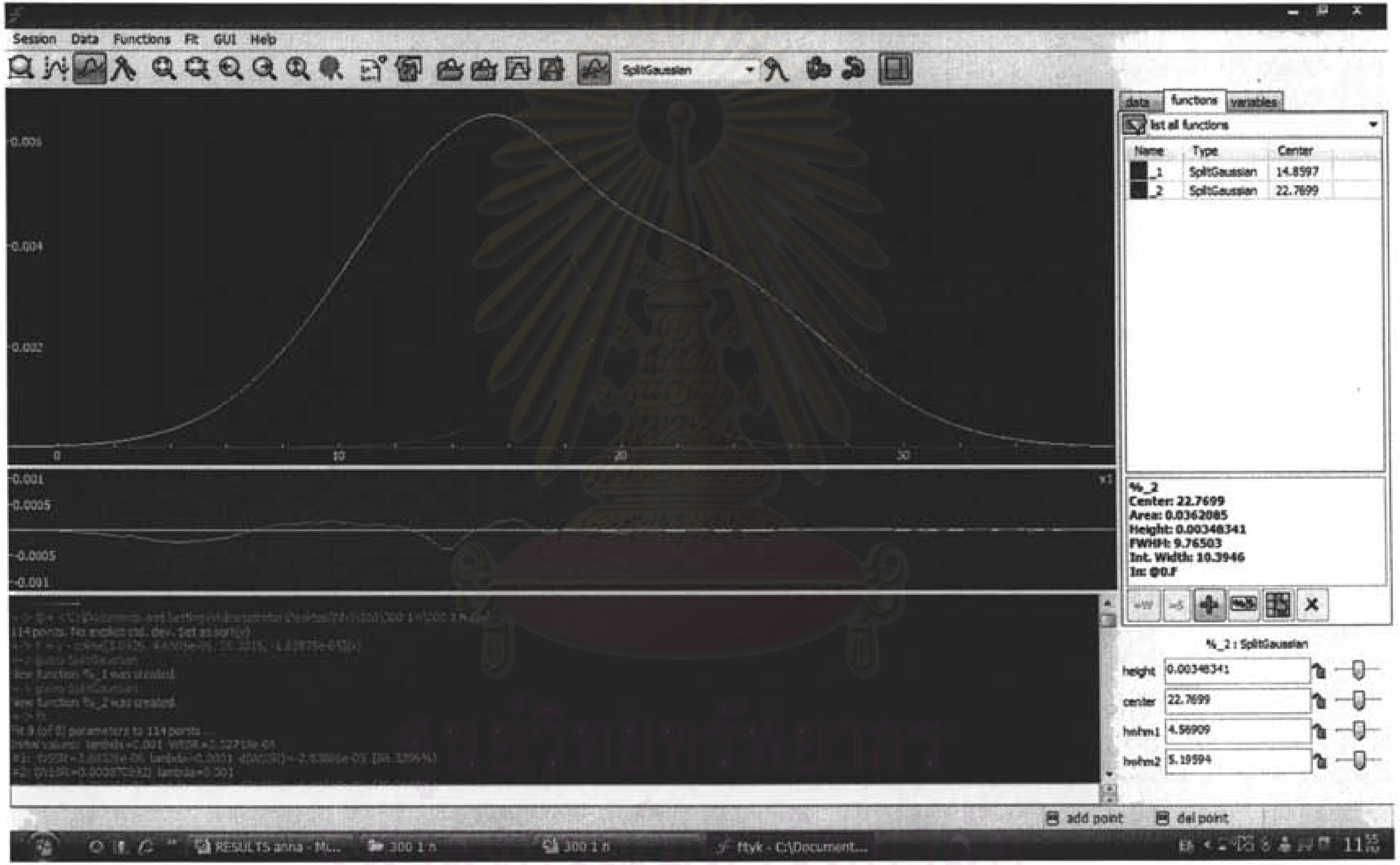
Name	Type	Center
%_1	SplitGaussian	47.5694
%_2	SplitGaussian	57.0556

%_2
Center: 57.0556
Area: 0.0438103
Height: 0.00323236
FWHM: 12.7328
Int. Width: 13.5537
In: @0.F

%_2 : SplitGaussian

height 0.00323236
center 57.0556
hwhm1 6.96063
hwhm2 5.77219

Figure F15 Curve fitting of acid site ratio of CoTS-1(150 T 3) from fitting program.



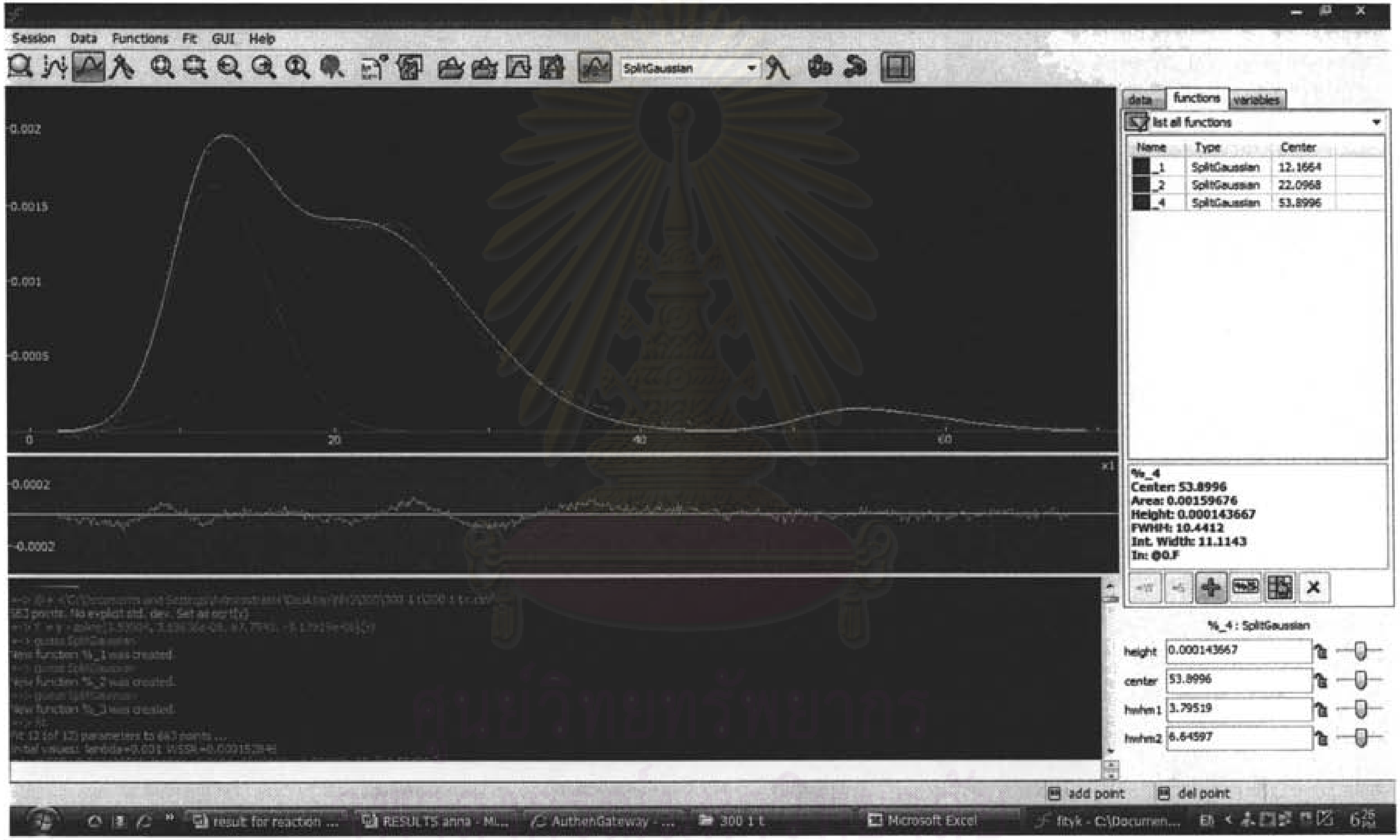
Name	Type	Center
_1	SplitGaussian	14.8597
_2	SplitGaussian	22.7699

%_2
Center: 22.7699
Area: 0.0362085
Height: 0.00348341
FWHM: 9.76503
Int. Width: 10.3946
In: @0.F

%_2 : SplitGaussian

height 0.00348341
center 22.7699
hwhm1 4.56909
hwhm2 5.19594

Figure F16 Curve fitting of acid site ratio of CoTS-1(300 N 1) from fitting program.



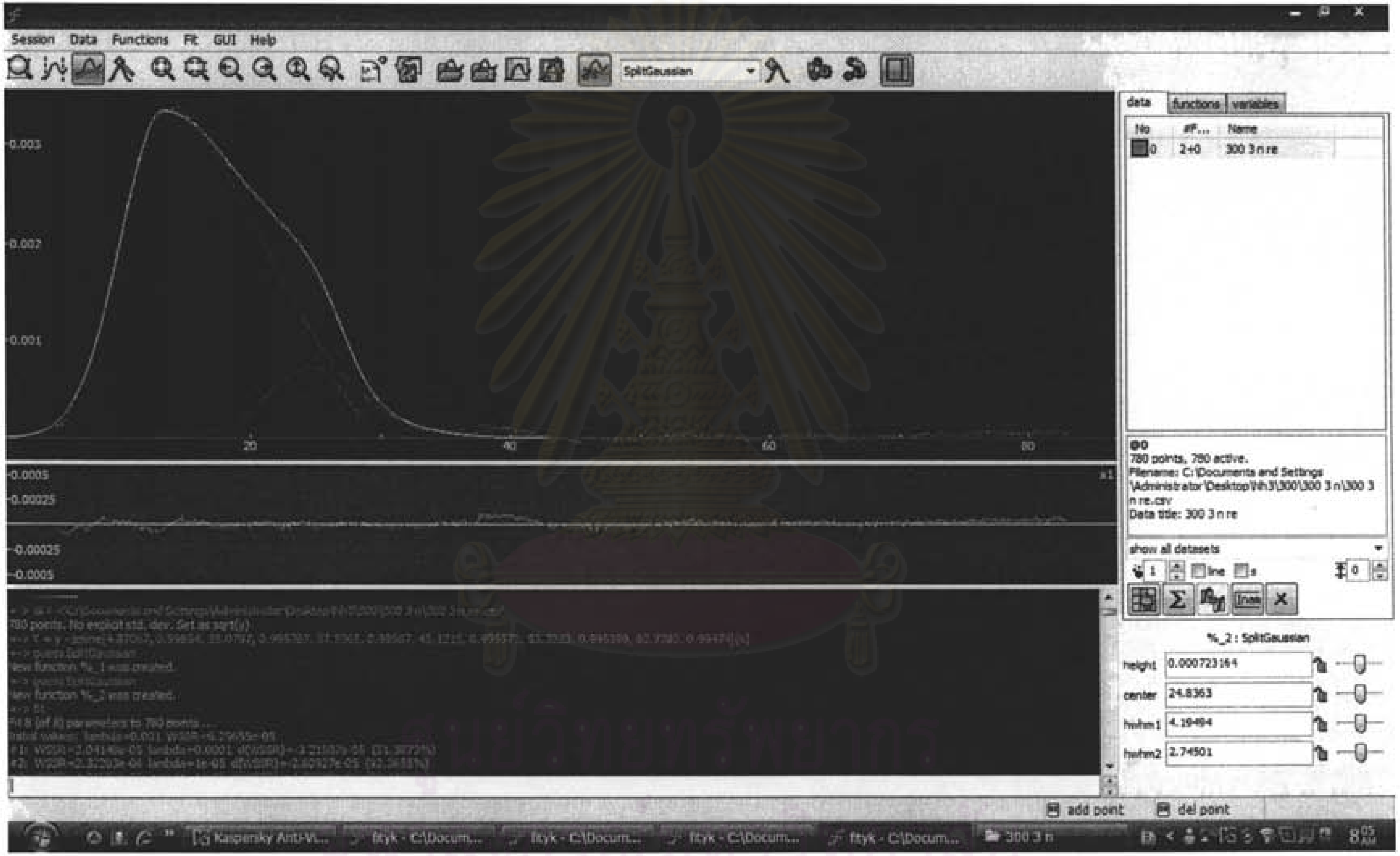
Name	Type	Center
_1	SplitGaussian	12.1664
_2	SplitGaussian	22.0968
_4	SplitGaussian	53.8996

%_4
Center: 53.8996
Area: 0.00159676
Height: 0.000143667
FWHM: 10.4412
Int. Width: 11.1143
In: @0.F

%_4 : SplitGaussian

height 0.000143667
center 53.8996
hwhm1 3.79519
hwhm2 6.64597

Figure F17 Curve fitting of acid site ratio of CoTS-1(300 T 1) from fitting program.\



```
780 points. No explicit std. dev. Set as sqrt(y)
New function %_1 was created.
New function %_2 was created.
Fit 8 (of 8) parameters to 780 points ...
```

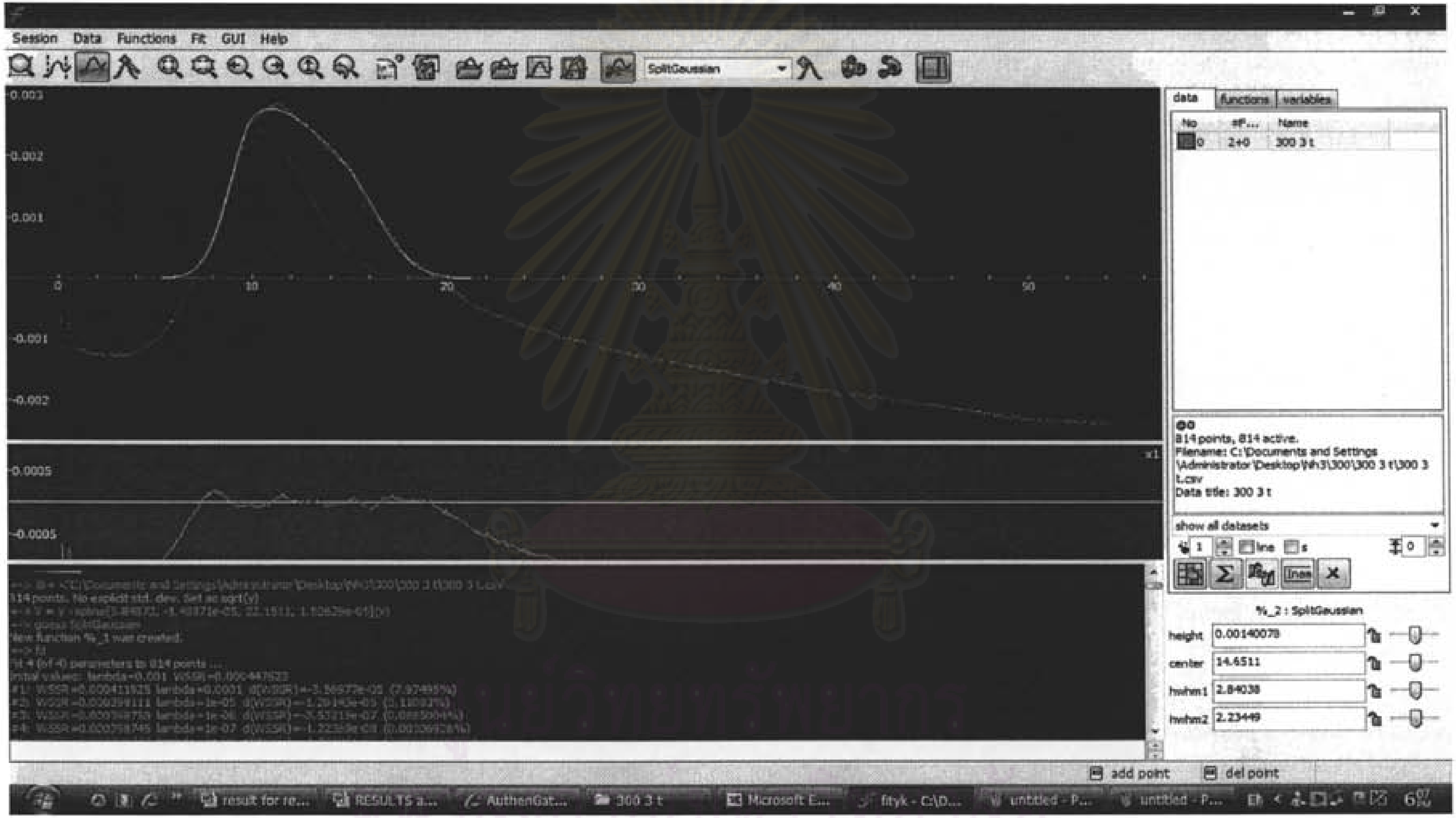
No	#F...	Name
0	2+0	300 3 n re

@0
780 points, 780 active.
Filename: C:\Documents and Settings\Administrator\Desktop\Nh3\300\300 3 n\300 3 n re.csv
Data title: 300 3 n re

%_2 : SplitGaussian

height1 0.000723164
center 24.8363
hwhm1 4.19494
hwhm2 2.74501

Figure F18 Curve fitting of acid site ratio of CoTS-1(300 N 3) from fitting program.



```
814 points. No explicit std. dev. Set as sqrt(y)
New function %_1 was created.
Fit 4 (of 4) parameters to 814 points ...
```

@0
814 points, 814 active.
Filename: C:\Documents and Settings\Administrator\Desktop\Nh3\300\300 3 t\300 3 t.csv
Data title: 300 3 t

show all datasets

%_2 : SplitGaussian

height: 0.00140078
center: 14.6511
hwhm1: 2.84038
hwhm2: 2.23449

Figure F19 Curve fitting of acid site ratio of CoTS-1(300 T 3) from fitting program.

APPENDIX G

CALCULATION OF METAL QUANTITY

Example of the calculation of the metal quantity in Co-TS-1 (50 T 1) catalyst

The XRF results were reported in the amount of metal oxide as shown in Table G1

Table G1 Data from XRF analysis.

Metal oxide	Concentration
Al_2O_3	0.106
SiO_2	98.641
TiO_2	1.092
Fe_2O_3	0.032
CoO	0.13

Molecular weights of the metal oxides are shown as follow:

Al_2O_3	101.963	Fe_2O_3	159.6922	SiO_2	60.0843
TiO_2	79.9	CoO	74.9331		

1. Mole of metal oxides

$$\text{Mole of } Fe_2O_3 = \frac{\text{weight of } Fe_2O_3}{\text{molecular weight of } Fe_2O_3}$$

$$\text{Mole of } Fe_2O_3 = \frac{0.032}{159.6922} = 2\times10^{-4} \text{ mole}$$

3. Mole of cation (e.g. potassium: Fe)

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

$$\begin{aligned}\text{Mole of Fe} &= (2)\times(2\times10^{-4})\\ &= 4\times10^{-4} \text{ mole}\end{aligned}$$

4. Mole percent of metal (e.g. potassium: Fe)

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

$$\text{Mole \% of Fe} = \frac{4\times10^{-4}}{1.658} = 0.00024 \text{ mole\%}$$

Calculated weight%, mole of metal oxide, mole of metal and mole% of cation are illustrated in Table G2.

Table G2 Calculated weight%, mole of metal oxide, mole of metal.

Metal oxides	weight%	mole of metal oxide	mole of cation	Mole% of metal
Al_2O_3	0.106	0.00104	0.002079	0.125377
SiO_2	98.641	1.64171	1.64171	98.99648
TiO_2	1.092	0.013667	0.013667	0.824136
Fe_2O_3	0.032	0.0002	0.000401	0.024167
CoO	0.13	0.001735	0.001735	0.104615
Total	99.9852	1.632	1.639	100

APPENDIX H

MATERIAL SAFETY DATA SHEET

Toluene

General

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

Physical data

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

Stability

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

Toxicology

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

Personal protection

Safety glasses, good ventilation.

Hydrogen peroxide

General

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

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

Molecular formula: H_2O_2

Physical data

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

Stability

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

Toxicology

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

Hazards Identification

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

Potential Health Effects

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

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

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

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

Personal protection

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

o-cresol

General

Synonyms: 2-cresol, *o*-cresylic acid, 1-hydroxy-2-methylbenzene, *o*-methylphenol, 2-methylphenol, *o*-toluol, 2-hydroxytoluene, *o*-hydroxytoluene
Molecular formula: C_7H_8O

Physical data

Appearance: colourless to light yellow liquid
Melting point: 32 - 34 °C
Boiling point: 191 °C
Vapour density: 3.72
Vapour pressure: 0.3 mm Hg at 20 °C
Specific gravity: 1.048
Flash point: 81 °C
Autoignition temperature: 598 °C

Stability

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

Toxicology

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

Personal protection

Safety glasses, gloves, good ventilation.

p-cresol

General

Synonyms: 1-hydroxy-4-methylbenzene, 4-methylphenol, p-cresylic acid, 4-cresol, *p*-hydroxytoluene, 4-hydroxytoluene, *p*-methylphenol, para-cresol, *p*-tolyl alcohol, *p*-toluol
Molecular formula: $CH_3C_6H_4OH$

Physical data

Appearance: crystals
Melting point: 34 °C
Boiling point: 202 °C
Vapour density: 3.7 (air = 1)
Vapour pressure: 0.1 mm Hg at 20 °C
Density (g cm^{-3}): 1.03
Flash point: 86 (closed cup)
Water solubility: moderate

Stability

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

Toxicology

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

Personal protection

Safety glasses, gloves, adequate ventilation.

Benzaldehyde

General

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

Molecular formula: C_6H_5CHO

Physical data

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

Stability

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

Toxicology

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

Personal protection

Safety glasses, adequate ventilation.

Titanium (IV) n-butoxide

General

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

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

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

Physical data

Boiling point: 310-314 °C

Flash point: 78 °C

Density : 1.486 g cm^{-3}

Toxicology

Irritating to eyes, respiratory system and skin.

Personal protection

Avoid contact with skin and eyes.

Tetrapropylammonium bromide

General

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

Physical data

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

Stability and reactivity

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

Hazardous decomposition

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

Potential health effect

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

First aid measure

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

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

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

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

Fire fighting measures

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

Hazardous product combustion

May emit Nitrogen oxides, Hydrobromic acid and Carbon monoxide.

Sodium chloride

General

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

Molecular formula: $NaCl$

Physical data

Appearance : colorless crystals or white powder
Melting point: 804 °C
Boiling point : 1413 °C
Vapor pressure : 1 mm Hg at 865°C
Specific gravity : 2.16 g cm^{-3}
Solubility in water : 35.7 g/100g at °C

Stability

Stable. Incompatible with strong oxidizing agents.

Toxicology

May cause skin, eye or respiratory irritation.

Personal protection

Not believed to present a significant hazard to health.

Sodium hydroxide

General

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

Physical data

Appearance : colorless white solid (often sold as pellets)
Melting point : 318 °C
Boiling point : 1390 °C
Vapor pressure : 1 mm Hg at 739 °C
Specific gravity : 2.12 g cm^{-3}
Water solubility : high (Note: dissolution in water is highly exothermic)

Stability

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

Toxicology

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

Personal protection

Safety glasses, adequate ventilation, Neoprene or PVC gloves.

Sodium silicate

General

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

Molecular formula: Na_4O_4Si

Physical data

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

Stability

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

Toxicology

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

Personal protection

Safety glasses, gloves.

Cobalt(II)nitrate hexahydrate

General

Synonyms: cobalt dinitrate hexahydrate, cobalt nitrate hexahydrate, nitric acid cobalt (+2) salt, cobaltous nitrate hexahydrate
Molecular formula: $Co(NO_3)_2\ 6H_2O$

Physical data

Appearance: red crystalline powder
Melting point: 56 °C
Density (g cm^{-3}): 1.54

Stability

Stable. Strong oxidizer - incompatible with reducing agents.

Toxicology

Harmful if swallowed or inhaled. Respiratory and eye irritant.

Personal protection

Safety glasses, adequate ventilation.

Ethanol

General

Synonyms: ethanol, grain alcohol, fermentation alcohol, alcohol, methylcarbinol, absolute alcohol, absolute ethanol, anhydrous alcohol, alcohol dehydrated, algrain, anhydrol, cologne spirit, ethyl hydrate, ethyl hydroxide, jaysol, jaysol s, molasses alcohol, potato alcohol, sekundasprit, spirits of wine.
Molecular C_2H_5OH

Physical data

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

Stability

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

Toxicology

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

Personal protection

Safety glasses. Suitable ventilation.

APPENDIX I

LIST OF PUBLICATION

Siya Udomchatchawan and Tharathon Mongkhonsi "Catalytic Study Of Cobalt Modified Tritium Silicates -1 In The Hydroxylation Of Toluene To Cresol By Hydrogen Peroxide,18th Thailand Chemical Engineering and Applied Chemistry Conference , Chonburi, Thailand, October, 2008,.Ref 031-KC-005-02 (oral presentation)

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Clean Energy Techology(cont.)

Book of Abstracts of the 18th Thailland Chemical Engineering and Applied Chemistry Conference
October 20-21, 2008, Pattaya, Thailand

Catalytic study of cobalt modified titanium silicates-1 in the hydroxylation of toluene to cresol by hydrogen peroxide

Siya Udomchatchawan, Suchitraporn Sakullimcharoen and Tharathon Mongkhonsi
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The present research investigates the hydroxylation of toluene to cresols over TS-1 and TS-1 promoted with cobalt (Co-TS-1) catalysts in a bubble reactor (total volume 40 ml) equipped with an overhead condenser. Hydrogen peroxide at different concentrations (3, 7.5 and 30 wt%) is used as the oxidant. Toluene is fed in the gaseous phase, using nitrogen as carrier gas, to the bottom of the bubble reactor contains catalyst and hydrogen peroxide solution. The reaction is carried out at 70 C and atmospheric pressure. Total volume of toluene fed is 1.5 ml over a period of 30 minutes and the total reaction time is 2 hours. The bubble reactor has an advantage over the conventional slurry reactor that it can compensate the hydrophobic nature of the catalyst, thus allowing more polar reactant (H_2O_2) to exist on the catalyst surface.

TS-1 and Co-TS-1 are synthesized using the hydrothermal technique with aging time 0, 1 and 3 days. It is found that aging TS-1 for 3 days produces the most selective catalyst toward cresols (o- and p-cresol) with a trace of benzaldehye. The different results are observed with the catalyst with 0 and 1 day aging which yield nearly 100% benzaldehye rather than cresol. The different behaviour is likely due to the catalyst with 3 days aging has a better crystallinity than the catalyst with 0 and 1 day aging. In addition, the addition of cobalt (Co-TS-1 catalyst) improve cresol selectivity by inhibiting the formation of benzaldehyde.

Keywords: ts-1, modified ts-1, toluene, cresol, bubble reactor, hydroxylation

CATALYTIC STUDY OF COBALT MODIFIED TITANIUM SILICALITES-1 IN THE HYDROXYLATION OF TOLUENE TO CRESOL BY HYDROGEN PEROXIDE.

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Abstract The present research investigates the hydroxylation of toluene to cresols over TS-1 and TS-1 promoted with cobalt (Co-TS-1) catalysts in a bubble reactor (total volume 40 ml) equipped with an overhead condenser. Hydrogen peroxide at different concentrations (3, 7.5 and 30 wt%) is used as the oxidant. Toluene is fed in the gaseous phase, using nitrogen as carrier gas, to the bottom of the bubble reactor contains catalyst and hydrogen peroxide solution. The reaction is carried out at 70 °C and atmospheric pressure. Total volume of toluene fed is 1.5 ml over a period of 30 minutes. The bubble reactor has an advantage over the conventional slurry reactor that it can compensate the hydrophobic nature of the catalyst, thus allowing more polar reactant (H_2O_2) to exist on the catalyst surface.

TS-1 and Co-TS-1 are synthesized using the hydrothermal technique with aging time 0, 1 and 3 days. It is found that aging TS-1 for 3 days produces the most selective catalyst toward cresols (o- and p-cresol) with a trace of benzaldehye. The different results are observed with the catalyst with 0 and 1 day aging which yield nearly 100% benzaldehye rather than cresol. The different behaviour is likely due to the catalyst with 3 days aging has a better crystallinity than the catalyst with 0 and 1 day aging. In addition, the addition of cobalt (Co-TS-1 catalyst) improve cresol selectivity by inhibiting the formation of benzaldehyde.

The main products, *o*-cresol, are formed in meso pore system whereas *p*-cresol, found in a is formed in micro pore system. In addition, Co cation promote the formation of ring oxidation product and inhibit the ring oxidation product at low H_2O_2 concentration (3 and 7.5 wt%).

1. Introduction

Cresols have a wide variety of uses including the manufacture of synthetic resins, tricresyl phosphate, salicylaldehyde, coumarin, and herbicides. cresol molecule has a methyl group substituted onto the benzene ring of a phenol molecule. There are three forms of cresols that are only slightly different in their chemical structure: ortho-cresol (o-cresol), meta-cresol (m-cresol), and para-cresol (p-cresol). These forms occur separately or as a mixture. An approximate breakdown of cresol and cresylic acid use is 20% phenolic resins, 20% wire enamel solvents, 10% agricultural chemicals, 5% phosphate esters, 5% disinfectants and cleaning compounds, 5% ore flotation, and 25% miscellaneous and exports.

The discovery of titanium silicalite-1 (TS-1) which is a zeolite of the pentasil family by Taramasso and co-worker in 1983 opened a new route for the catalysis and catalytic reaction. The new material has attracted a great deal of attention. Structurally, the titanium in TS-1 isomorphously replaces silicon in a tetrahedral site of the MFI silicalite lattice. As such, it combines the advantages of the high coordination ability of Ti^{4+} ions with the hydrophobicity of the silicalite framework, while retains the spatial selectivity and specific local geometry of the active sites of molecular sieve structure.

There are many types of reactor using for hydroxylation such as catalytic membrane reactor [1] fixed bed and recycle reactor [2] glass batch reactor [3] and electrochemical cells reactor [4] From former researcher [5] studied in the bubble reactor which are widely used in chemical industry where heterogeneous gas-liquid or gas-solid reaction take place, particularly, in which the liquid phase controls mass transfer processes due to the relative insolubility of gases. Therefore, the bubble reactor is chosen as reactor in present work.

[6] reported that the metal modified TS-1 catalysts gave a higher phenol conversion rate than TS-1. Another work has reported that loading transition metals to TS-1 up to a level still maintained the MFI structure [7].

The aim of the present research is to investigate the metal modified TS-1 catalysts by adding Co during the synthesis step by a hydrothermal method. In addition, the oxidation properties of metal modified TS-1 and effect of treatment of catalysts in the hydroxylation of toluene with H_2O_2 as the oxidizing agent have never been studied before.

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2. Experimental

2.1 Catalyst preparation

The sources of metals 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 of Si/Ti is set at 50 and Si/Co is set at 50 and 150, respectively. The recipies 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 modied by adding Co with 3 days aging are named Co-TS-1(150) pretreated and no pretreated respectively.

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			**Solution A2**		
$Ti[O(CH_2)_3CH_3]_4$	2.2085	g	$Ti[O(CH_2)_3CH_3]$	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			
H2SO4 (conc.)	1.55	ml			

Firstly, a gel mixture is prepared by adding solution A-1 and solution B-1 into solution C-1 dropwise 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 3 days, followed by cooling the mixture to room temperature in the autoclave. The product crystals are washed with de-ionized water by a centrifuge. Then the crystals are dried in an oven at 110°C after that they are calcined in an air stream at 550°C and held at that temperature for 7 h, by heating them from room temperature to 550°C at a heating rate of 8.6 °C/min. For a catalyst sample, the catalyst is treated with 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 at 540°C for 7 h in static air.

2.2 Catalyst characterization

The crystallinity and X-ray diffraction patterns of the catalysts were performed 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 with Ni filter. Scans 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 Siemens SRS3400.

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

2.3 Catalytic Performance

The procedures are described in the detail below. 1 g of catalyst powder, hydrogen peroxide and a magnetic bar were filled in the bubble reactor. Then, the reactor was heated up temperature to 70 °C. Adjust the outlet pressure of nitrogen to 1.5 bars and turn on the on-off valve to allow nitrogen gas to pass through the evaporating system. Start the reaction by injecting certain an amount of liquid toluene to the evaporating system. The gas mixture passes through the mixture containing the catalyst and hydrogen peroxide, where the hydroxylation of alkyl benzene reaction to took place. Analyze the product sample by placing the reactor into the cool bath in order to stop the reaction. Mix the liquid mixture with 40 ml of ethanol and stir until the liquid mixture became a homogeneous phase. After that, centrifuge the mixture in order to separate the catalyst from the liquid solution. The liquid product was analyzed by the FID gas chromatography. The chromatogram data were converted into mole of products using a calibration curve

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3. Result and discussion

3.1 Characterization of catalysts

X-ray diffraction (XRD)

The XRD spectra of TS-1 and modified with Co (Co-TS-1) are shown in Figure 1. All samples 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 pattern of anatase 2 theta ≈ 25.3° does not appear which shows anatase does not exist in the TS-1 and Co-TS-1 synthesized using TPABr as the template[9]. The single peaks at 2 theta ≈ 24.4 and 26° indicate an orthorhombic symmetry typical of TS-1 with a framework Si/Ti < 100 [10].

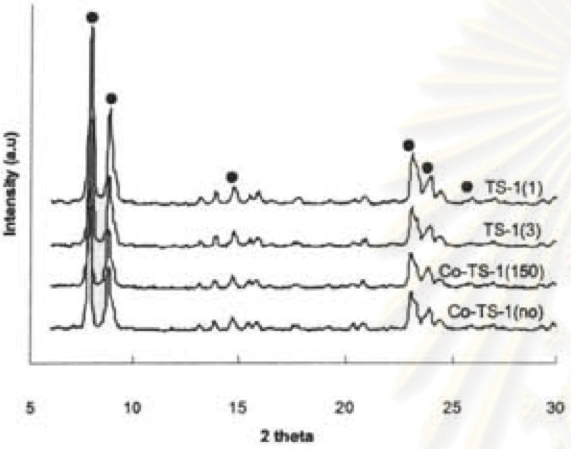

Figure 1. XRD pattern of TS-1 and modified TS-1

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 [10]. 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 incorporated into the framework [9-11].

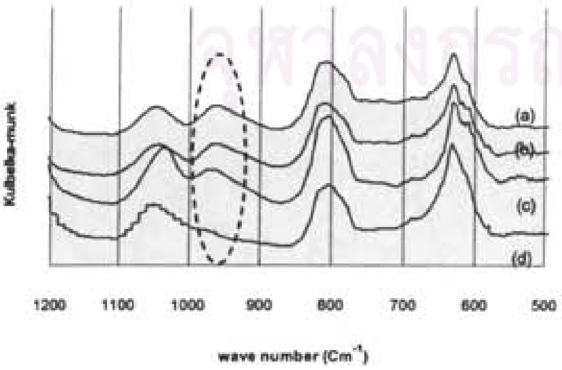

Figure 2. IR spectra of TS-1 and modified TS-1 : TS-1(1) (a), TS-1(3) (b), Co-TS-1(treated) (c) and Co-TS-1(no treatment) (d).

Determination of surface area by BET technique

It is found that the surface areas of all catalysts investigated are in the range 340-390 m^2/g.

3.2 The catalytic reaction of hydroxylation of toluene

The conversion of toluene and product seleoxtivites obtained from the hydroxylation of toluene at 70°C with TS-1 and Co-TS-1 are reported in Figures 3 and 4, respectively. Co-TS-1(treated) can not used with 30% H_2O_2 because it causes the rapid and vigorous decomposition of H_2O_2. Because of this reason, no experimental data on 30% H_2O_2 concentration of Co-TS-1(treated) is absent.

The results in figure 3 show that at the concentrations of H_2O_2 at 7.5% and 3% do strongly affect conversion of toluene for all catalysts except TS-1 (1 day). When the concentration of H_2O_2 is raised to 30%, each catalyst behaves differently. TS-1 (3 day) shows a large increase in toluene conversion while TS-1 (1 day) and Co-TS-1 (no treatment) show a significant drop.

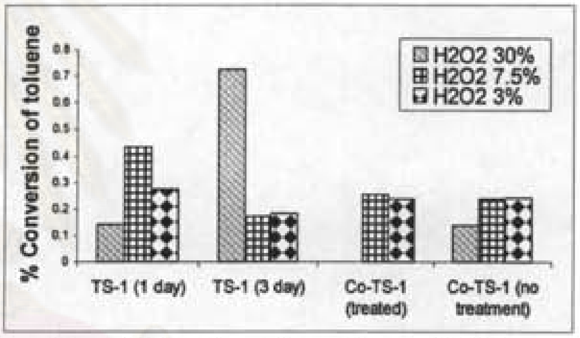

Figure 3. The hydroxylation of toluene at 70°C

The selectivity and product selectivity of each catalyst at different concentrations of H_2O_2 are schematically summarized in Figure 4. TS-1 (1 day) and TS-1 (3 day) produce mixtures of side chain oxidation and ring hydroxylation products at every H_2O_2 concentrations used in this study. The addition of Co accompany with the treatment with the nitric acid solution makes the catalyst behaves differently. Although the treatment is reported to be a technique that can increase the catalytic activity of TS-1 in the hydroxylation of benzene to phenol, this technique can not be used with Co-TS-1 used in the hydroxylation of toluene to cresols. The treatment causes the catalyst (Co-TS-1(treated)) produces only benzaldehyde, the undesired product in this work while the catalyst without any treatment (Co-TS-1(no treatment)) yields only cresols.

The different products formed between Co-TS-1(treated) and Co-TS-1(no treatment) is possibly due to the treatment with the nitric acid solution removes some species that block the active site that prefers the formation of benzaldehyde and destroy the active site that prefers the formation of cresols.

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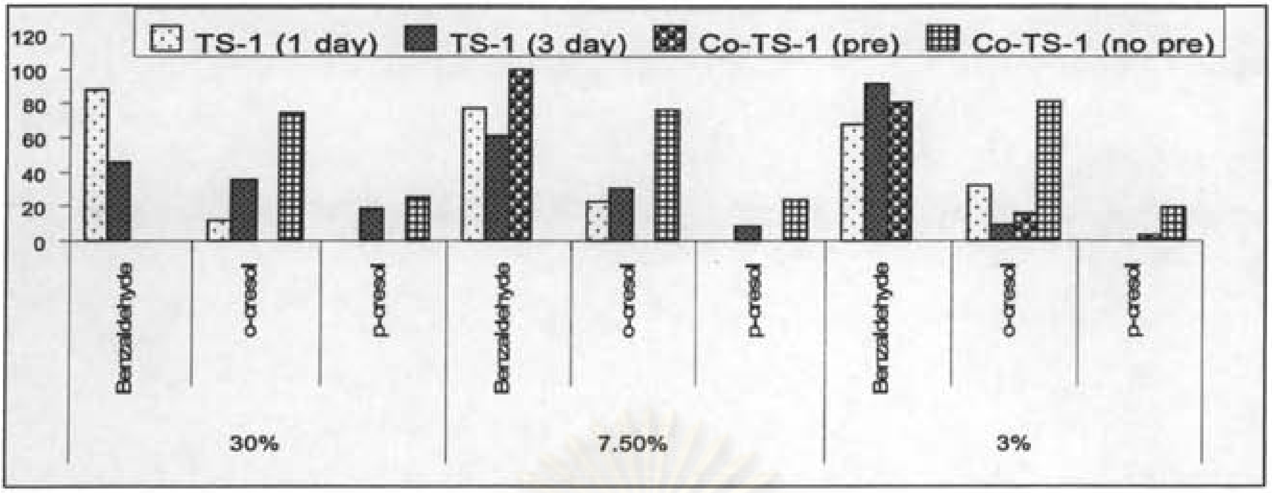

4. Conclusion

The research found that the incorporation of Co to TS-1 can yield catalysts which can produce either the methyl group side chain oxidation product (benzaldehyde) or the ring hydroxylation products (o-cresol and p-cresol) in the hydroxylation of toluene at 70°C. The treatment with the solution of nitric acid of Co-TS-1 produces a catalyst (Co-TS-1 (treated)) which yield only benzaldehyde at 7.5% H_2O_2 concentration. On the contrary, at the same condition, the catalyst without any treatment (Co-TS-1 (no treatment)) produces only cresols regardless of H_2O_2 concentration.

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