ปฏิกิริยาไฮดรอกซิเลชันของอัลคิลเบนซีนในเครื่องปฏิกรณ์แบบฟองแก๊สด้วยตัวเร่งปฏิกิริยา TS-1 และตัวเร่งปฏิกิริยา TS-1 ที่ได้รับการปรับปรุง

นางสาวสุจิตราภรณ์ สกุลลิ้มเจริญ

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HYDROXYLATION OF ALKYL BENZENES IN A BUBBLE REACTOR USING TS-1 AND MODIFIED TS-1 CATALYSTS

Miss Suchitraporn Sakullimcharoen

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
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Thesis Title	HYDROXYLATION OF ALKYL BENZENES IN A BUBBLE REACTOR USING TS-1 AND MODIFIED TS-1 CATALYSTS
By	Miss Suchitraporn Sakullimcharoen
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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สุจิตราภรณ์ สกุลลิ้มเจริญ: ปฏิกิริยาไฮดรอกซิเลชันของอัลคิลเบนซีนในเครื่องปฏิกรณ์แบบฟองแก๊สด้วยตัวเร่งปฏิกิริยา TS-1 และตัวเร่งปฏิกิริยา TS-1 ที่ได้รับการปรับปรุง (HYDROXYLATION OF ALKYL BENZENES IN A BUBBLE REACTOR USING TS-1 AND MODIFIED TS-1 CATALYSTS.) อ. ที่ปรึกษา: รศ.ดร.ธราธร มงคลศรี, 98 หน้า

งานวิจัยนี้ได้ศึกษาปฏิกิริยาไฮดรอกซิเลชันของอัลคิลเบนซีนในเครื่องปฏิกรณ์แบบฟองแก๊สโดยใช้ตัวเร่งปฏิกิริยา TS-1 และ TS-1 ที่ได้รับการปรับปรุง และใช้ไฮโดรเจนเปอร์ออกไซด์เป็นตัวออกซิไดซ์ ภายในเครื่องปฏิกรณ์แบบฟองแก๊ส เบนซินถูกป้อนเข้าไปในวัฏภาคแก๊ส ไฮโดรเจนเปอร์ออกไซด์ในวัฏภาคของเหลว และตัวเร่งปฏิกิริยาที่แช่ในไฮโดรเจนเปอร์ออกไซด์อยู่ในวัฏภาคของแข็ง เส้นทางการเกิดเป็นผลิตภัณฑ์ของปฏิกิริยาไฮดรอกซิเลชัน มีอยู่ 2 เส้นทาง คือ การเกิดออกซิเดชันที่วงแหวนโดยตรงซึ่งเป็นเส้นทางการเกิดที่ต้องการ และการเกิดออกซิเดชันที่หมู่อัลคิล ปฏิกิริยาไฮดรอกซิเลชันของโทลูอีนได้เบนซัลดีไฮด์ (ออกซิเดชันที่วงแหวน) และครีซอล (ออกซิเดชันที่หมู่อัลคิล) เป็นผลิตภัณฑ์ ในกรณีของเอทิลเบนซีนพบพบว่าเกิดอะซีโตฟีโนนและ1-ฟีนิล เอทานอล ในปริมาณน้อย ซึ่งเป็นผลิตภัณฑ์ที่ได้จากการออกซิเดชันที่หมู่อัลคิล เบนซัลดีไฮด์และออโทครีซอลซึ่งผลิตภัณฑ์หลักของปฏิกิริยาไฮดรอกซิเลชันของโทลูอีนพบว่าเกิดในระบบรูพรุนขนาดกลาง (meso pore) ในขณะที่ Al-TS-1 และ Co-TS-1 ที่ความเข้มข้นไฮโดรเจนเปอร์ออกไซด์สูงเกิดพาราครีซอลซึ่งพบในระบบรูพรุนขนาดเล็ก (micro pore) สำหรับโลหะตัวที่สองโคบอลต์และวานาเดียมพบว่าเพิ่มการเกิดเป็นผลิตภัณฑ์ที่ได้จากการออกซิเดชันที่วงแหวนและยับยั้งการเกิดออกซิเดชันที่หมู่อัลคิล ในส่วนของไอออนบวกอลูมิเนียมพบว่าที่ความเข้มข้นไฮดรอกเจนเปอร์ออกไซด์สูง (30 wt%) จะส่งเสริมการเกิดออกซิเดชันที่วงแหวนและยับยั้งการเกิดออกซิเดชันที่วงแหวนที่ความเข้มข้นไฮดรอกเจนเปอร์ออกไซด์ต่ำ (3 และ 7.5 wt%) ในส่วนของปฏิกิริยาไฮดรอกซิเลชันของเอทิลเบนซีนพบว่าเกิดผลิตภัณฑ์ในปริมาณน้อยเนื่องจากค่าการละลายของเอทิลเบนซีนในน้ำต่ำซึ่งนำไปสู่การดูดซับในปริมาณน้อยบนพื้นผิวตัวเร่งปฏิกิริยา

ภาควิชา.............วิศวกรรมเคมี.......... ลายมือชื่อนิสิต สุจิตราภรณ์ สกุลลิ้มเจริญ..........
สาขาวิชา............วิศวกรรมเคมี.......... ลายมือชื่ออาจารย์ที่ปรึกษา..........................
ปีการศึกษา..........2550....................

##4970639521: MAJOR CHEMICAL ENGINEERING
KEY WORD: TS-1/ MODIFIED TS-1/ ALKYL BENZENES/ TOLUENE/ ETHYL BENZENE/ BUBBLE REACTOR/ HYDROXYLATION

SUCHITRAPORN SAKULLIMCHAROEN: HYDROXYLATION OF ALKYL BENZENES IN A BUBBLE REACTOR USING TS-1 AND MODIFIED TS-1 CATALYSTS. THESIS ADVISOR: ASSOC.PROF. THARATHON MONGKHONSI, Ph.D. 98 pp.

This research has investigated the hydroxylation of alkyl benzenes (toluene and ethyl benzene) over TS-1 and modified TS-1 (Al-TS-1, Co-TS-1, Fe-TS-1 and V-TS-1) catalysts in a bubble reactor using hydrogen peroxide (3, 7.5 and 30 wt%) as an oxidant. In the reactor, reactant (toluene or ethyl benzene) was fed in gas phase, hydrogen peroxide was in aqueous phase, and catalyst which was immersed in hydrogen peroxide solution, was solid. The routes of product formation from the hydroxylation reaction have two paths, the ring oxidation that produces interested products, and another path is the side chain oxidation. The toluene hydroxylation gives cresol (ring oxidation product) and benzaldehyde (side chain oxidation product). In the case of hydroxylation of ethyl benzene acetophenone and 1-phenyl ethanol (both are side chain oxidation products) are observed in trace amount. The main products, benzaldehyde and *o*-cresol, are formed in meso pore system whereas *p*-cresol, found in a significant amount of Al-TS-1 and Co-TS-1 at 30 wt% H_2O_2, is formed in micro pore system. Co and V cation enhance the formation of ring oxidation product and inhibit the formation of side chain oxidation product. In addition, at high H_2O_2 concentration (30 wt%) Al 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%). The products from hydroxylation of ethyl benzene are found in trace amount due to low solubility in water which leads to a fewer amount of ethyl benzene on catalyst surface.

Department……Chemical Engineering… Student's signature. Suchitraporn Sakullimcharoen
Field of study…Chemical Engineering… Advisor's signature……………………
Academic year…..2007…………………

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Finally, she would like to dedicate the achievement of this work to her parents (Mr. Saravut Sakullimcharoen, Ms. Pranee Chantarawongsakul) 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. Cresols also serve as components of degreasing compounds in textile scouring and paintbrush cleaners as well as fumigants inphotographic developers and explosives. Cresols also function as antiseptics, disinfectants, and parasiticides in veterinary medicine. 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.

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

The hydroxylation reaction by hydrogen peroxide with a heterogeneous catalytic system has advantages over homogeneous system since it allows simple separation and recovery of catalysts from reaction mixture. Therefore, development of heterogeneous catalysts is particularly attractive. Recently, many researchers have attempted to improve catalytic properties. Many second metals such as Al, V, Cr, Fe, Co and Ru are introduced into TS-1 catalyst for improve its performances. Laufer and Hoelderich (2001) found that Pd/Pt/TS-1 catalyst could improve the selectivity of propylene oxide in the direct oxidation of propylene. Ma et al. (2005) studied the transesterification of dimethyl oxalate with phenol over stannum modified TS-1 and found that the Sn-modified TS-1 catalysts had fewer Lewis acid sites than the unmodified TS-1 but its catalytic activity was increased greatly by the interaction of Sn with Ti–O–SiO_3 weak Lewis acid centers. Gas-phase epoxidation of propylene over small gold ensembles on TS-1 was investigated by Taylor et al., (2005). They found that low gold loadings resulted in an inherently small number of very active sites and forcing the gold loading to higher values resulted in poor activity and stability.

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 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.

Previously, the hydroxylation is performed in liquid phase that the catalyst surface is mostly covered by the adsorbed alkyl benzene 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 alkyl benzene 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, alkyl benzene vapor is bubble through the slurry. Due to the concentration of alkyl benzene is reduced and alkyl benzene is introduced secondly, the portion of the catalyst surface covered by H_2O_2 is expected to be higher than feeding alkyl benzene in liquid phase.

In the present work, the objective is to study oxidation properties of TS-1 and metal modified TS-1 catalysts (Al-TS-1, Co-TS-1, Fe-TS-1 and V-TS-1) pretreatment with HNO_3 solution in the hydroxylation of alkyl benzene by hydrogen peroxide as an oxidant in a bubble flow reactor. The research has been scoped as follows:

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

2) The ratio of synthesized catalysts is 50 for Si/Ti and 150 for Si/M, where M is second metal.

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

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

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

- Determination of morphology of catalysts by scanning electron microscopy (SEM)

5) Investigate catalytic behavior of synthesized catalysts are evaluated by three phase hydroxylation alkyl benzenes (toluene and ethyl benzene) using hydrogen peroxide as an oxidant in bubble reactor at 70 °C.

6) Influence of concentration of hydrogen peroxide that affect on synthesized catalysts in hydroxylation of alkyl benzenes.

This present work is organized as follows:

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

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

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

The characterization of synthesized catalysts and results of hydroxylation of alkyl benzenes, 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.

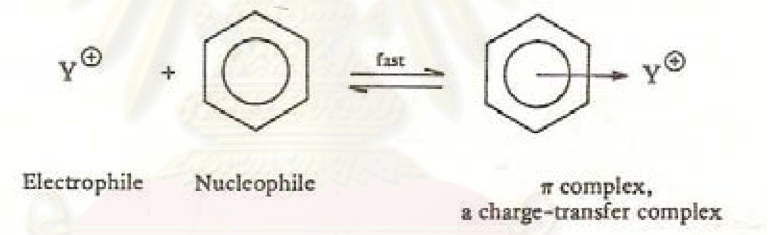
CHAPTER II

THEORY AND LITERATURE REVIEWED

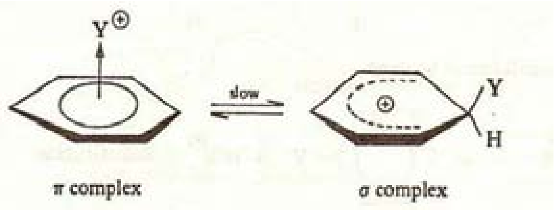
2.1 Electrophilic aromatics substitution

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.

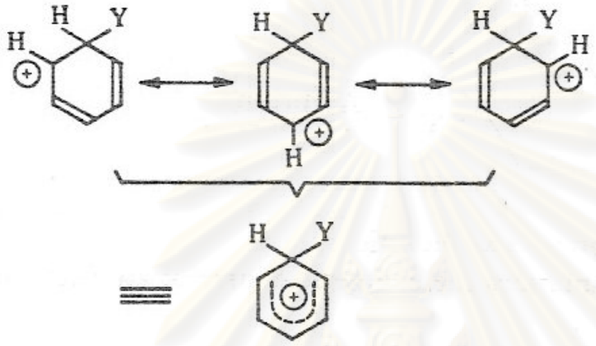
A π complex is formed. The electrophilic reagent $Y^{\oplus}$ is attracted by the nucleophilic π-electron cloud of benzene and is loosely held.

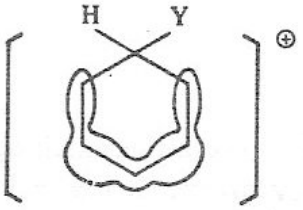


A conjugated carbonium ion is formed. The electrophilic reagent $Y^{\oplus}$ in the π complex attaches to a particular carbon atom, which thereby becomes sp^3-hybridized. The positive charge is delocalized over the other five carbons which are still in the sp^2 state and remain in one plane with the 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.



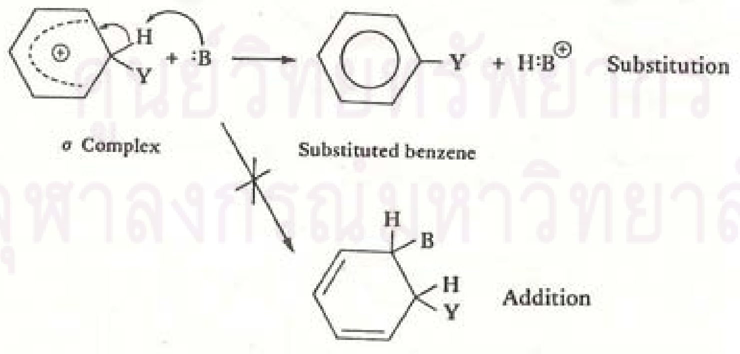
The σ complex is a resonance hybrid of three contributing structures. The positive charge is mainly in *o* or *p* positions.





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.



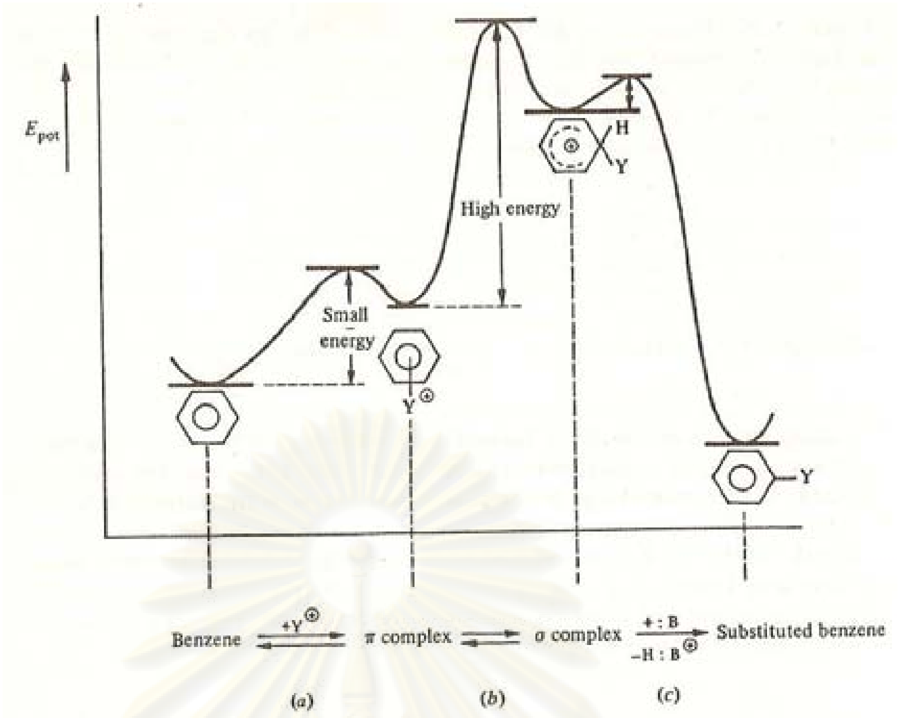


Figure 2.1 Energy profile of electrophilic aromatic substitution on benzene ring. (Zlatkis et al., 1985)

This step requires only a small E_{act}, and is exothermic. The energy profile in Figure 2.1 summarizes the energetic course of an electrophilic aromatic substitution on benzene.

2.2 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).

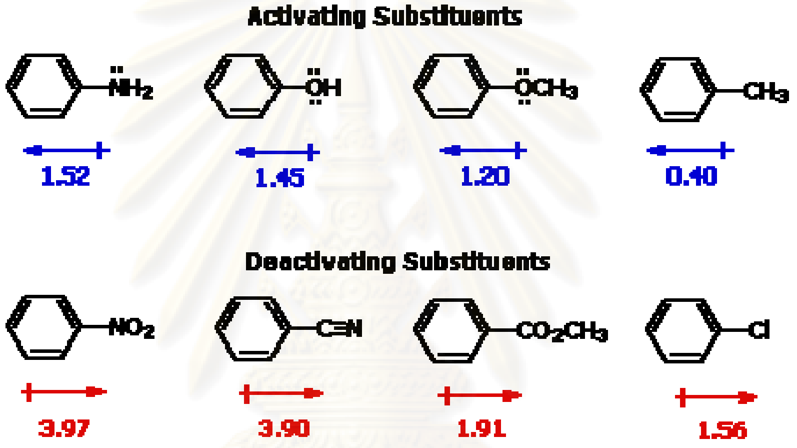


Figure 2.2 Diagram of electron donating substituents (blue dipoles) activate the benzene ring and electron withdrawing substituents (red dipoles) deactivate the ring. (www.cem.msu.edu/~reusch/VirtualText/benzrx1.htm#benz5)

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.

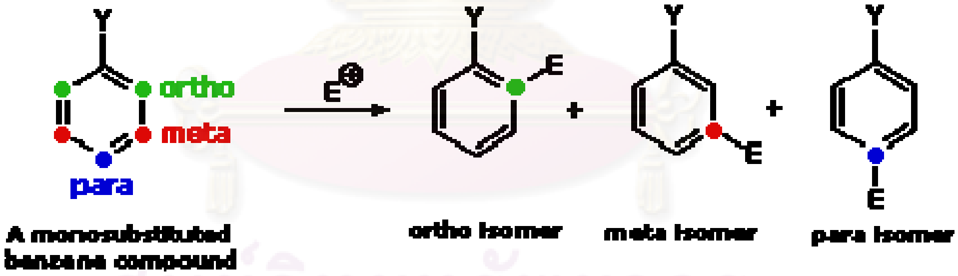


Figure 2.3 The position of monosubstituted electrophile on benzene ring. (www.cem.msu.edu/~reusch/VirtualText/benzrx1.htm#benz5)

The manner in which specific substituents influence the orientation of electrophilic substitution of a benzene ring is shown in the following interactive diagram (Figure 2.4). 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.

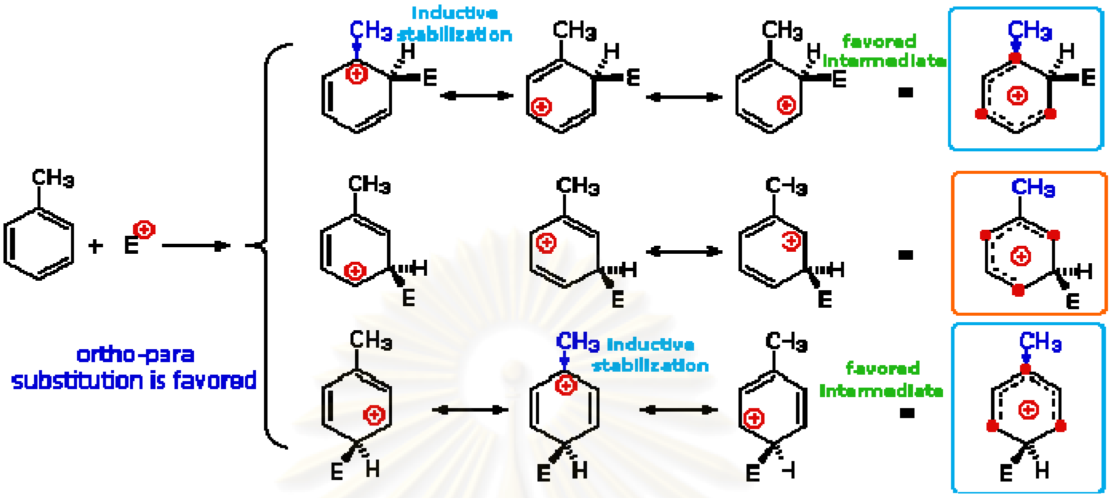


Figure 2.4 The delocalized positive charge on the benzenonium intermediates generated by bonding to the electrophile.
(www.cem.msu.edu/~reusch/VirtualText/benzrx1.htm#benz5)

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
$–O^{(–)}$ –OH –OR $–OC_6H_5$ $–OCOCH_3$	$–NH_2$ $–NR_2$ $–NHCOCH_3$ –R $–C_6H_5$	$–NO_2$ $–NR_3^{(+)}$ $–PR_3^{(+)}$ $–SR_2^{(+)}$ $–SO_3H$ $–SO_2R$	$–CO_2H$ $–CO_2R$ $–CONH_2$ –CHO –COR –CN	–F –Cl –Br –I $–CH_2Cl$ $–CH=CHNO_2$

2.3 Hydroxylation of aromatic hydrocarbon

2.3.1 Hydroxylation of benzene

Hydroxylation is any chemical process that introduces one or more hydroxyl groups (-OH) into a compound (or radical) thereby oxidizing it. For hydroxylation of benzene as shown in Figure 2.5 that has phenol is a product and para-benzoquinone, catechol and hydroquinone as secondary products

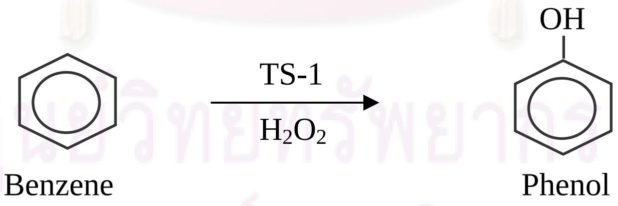


Figure 2.5 Hydroxylation of benzene to phenol over TS-1 catalyst.

From previous work, Kumar et al. (1999) studied enhancement in the reaction rates in the hydroxylation of aromatics over TS-1/H_2O_2 under solvent-free triphase conditions. They found that significant enhancement (3-10 times) in the reaction rates in the hydroxylation of water immiscible aromatic compounds like benzene, anisole and toluene when compared with bi-phase condition in the presence of a co-solvent.

In the case of substituted benzenes (anisole and toluene) para-hydroxy product was predominantly obtain under triphase condition. However, in biphase the formation of ortho-isomer was preferred. The probable factors responsible for enhancement in activity and change in region-selectivity are relative hydrophobic nature and restricted pore dimensions of titanium silicate TS-1, diffusive resistance faced by the substrate with an organic co-solvent in biphase while such a resistance is minimized in triphase.

Bengoa et al. (1998) studied influence of TS-1 structural properties and operation conditions on benzene catalytic oxidation with H_2O_2. They found that small changes in the preparation lead to the presence of extra framework. The synthesis conditions must be controlled carefully to get pure TS-1, since the presence of extra framework titanium inhibits benzene hydroxylation. Both of catalyst, pure TS-1 and extra framework titanium, have the same MFI structure. In the benzene hydroxylation reaction using TS-1 prepared by the method of Thangaraj et al., the presence of sodium traces in the solid or methanol in reaction mixture change the activity drastically. These results were attributed to a deactivation of active Ti^{4+} sites. From this research, novel evidence is presented for the existence of different types of framework Ti^{4+} in TS-1 prepared by the method of Thangaraj et al.

Pirutko et al. (2001) studied preparation and catalytic study of metal modified TS-1 in the oxidation of benzene to phenol by N_2O. The second metals (Fe, Al, Ru, Co, V, Cr) are introduced into the TS-1 matrix at stage hydrothermal synthesis. In all case, the chemical composition of initial gel was calculated to provide 1 wt.% of the metal in TS-1. This condition is satisfied for Fe, Al and Ru. With Co and Cr, the concentration is higher (1.6 and 1.9 wt.%) and with V is lower (0.14wt.%) than the calculated value. The results for Fe-TS-1 containing 0.95 wt.% are 3.84 mol% of exit reaction mixture and 98% phenol selectivity. One may see that all M-TS-1 samples are inert and not even trace amounts of phenol are produced in their presence. Only the Al-containing sample exhibits a detectable but very low activity. However, this can hardly be interpreted as an intrinsic catalytic activity of Al species.

2.3.2 Hydroxylation of toluene

There are many researchers who attempt to modified catalysts for hydroxylation of aromatic compound. Bartoli et al. (2002) studied unusual efficiency of a non-heme iron complex as catalyst for the hydroxylation of aromatic compounds by hydrogen peroxide comparison with iron porphyrins. The non-heme iron complex, $Fe(TPAA)(ClO_4)_2$, is a bad catalyst for the epoxidation of alkenes such as cyclooctene, cyclohexene and cis-stilbene and for the hydroxylation of alkanes such as adamantane by H_2O_2, when compared to the iron porphyrin $Fe(TDCPN_5P)Cl$. At the opposite, they found $Fe(TPAA)(ClO_4)_2$ is a much better catalyst for the hydroxylation of arenes by H_2O_2 in its presence, anisole, toluene, ethylbenzene, benzene and chlorobenzene are transformed into the corresponding phenols, with respective yields of 53, 17, 24, 22 and 13% based on H_2O_2. The main products alkylphenols (ortho-, meta- and para-substituted phenol) of toluene was found.

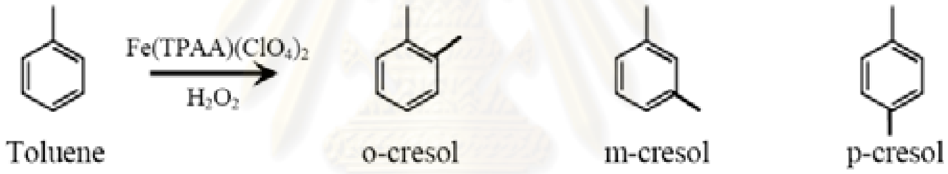


Figure 2.6 Hydroxylation of toluene over $Fe(TPAA)(ClO_4)_2$ catalyst.

2.3.3 Hydroxylation of ethylbenzene

Effective utilization of ethylbenzene, available in the xylene stream of the petrochemical industry to more value added products is an interesting proposition. Well known are the isomerization of ethylbenzene to xylenes and dehydrogenation to styrene monomer. Oxidation of ethylbenzene has not drawn much attention due to the complexity of the products that could be formed, particularly in the vapor phase catalytic oxidation using molecular oxygen. Mal et al. (1996) studied oxidation of ethylbenzene over Ti-, V- and Sn-containing silicalites with MFI structure. They take an interest in the course of reaction, which has more than one possibility. They found that oxidation of ethylbenzene to the different products can take place in two ways.

One is the aromatic ring hydroxylation under which the hydroxylation at the para position is preferred to some extent to the ortho position. The other is the side chain (ethyl group) oxidation at primary and secondary carbon atoms. The primary and secondary carbinols formed from the side chain oxidation undergo further oxidation to the respective aldehyde and ketone. The side chain oxidation at the secondary carbon predominates over the primary carbon atom. In the case of TS-1, the oxidation does not occur at the primary carbon atom. Nevertheless, between the two path ways, the product distribution indicates that the side chain product selectivity is around 4 to 5 times that of aromatic ring oxidation products. The turn over number (TON) of ethylbenzene over TS-1 and VS-1 are 8.4 and 4.9, respectively whereas over Sn-Sil-1 it is 15.4. The product selectivity shows that in the side chain oxidation of ethylbenzene over TS-1 gives 1-phenylethanol (33%) and acetophenone (41.4%) whereas aromatic ring gives o-hydroxy ethylbenzene (10.6%) and p-hydroxy ethylbenzene (12.4%). Moreover, they studied effect of H_2O_2 concentration and influence of ethylbenzene concentration. They found, the lower concentration of H_2O_2 results in a lower TON of ethylbenzene and little effect of solvent (acetronitrile) dilution on the product distribution was observed.

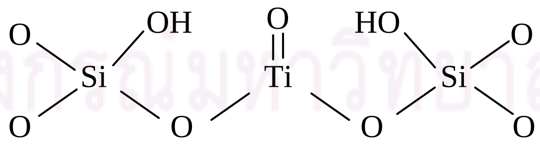
2.4 Titanium silicalite – 1

Titanium silicalite is the most 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 particularly, extra-framework massive Ti-oxides as well as other contaminants cause undesirable side reactions and consequence losses of activity and selectivity of the catalyst.

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 alkyl benzene and (4) adsorption of reactants on catalysts. 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 in section 3.4.

3.1 Catalyst preparation

3.1.1 Chemicals

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

Table 3.1 The 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
Vanadium(III)chloride	Analytical	Fluka
Iron(III)chloride hexahydrate	Analytical	Merck
Aluminium(III)nitrate nonahydrate	Analytical	APS

3.1.2 Preparation Procedures

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

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

Solution for the gel preparation			Solution for decant-solution preparation		
Solution A1			Solution A2		
$Ti[O(CH_2)_3CH_3]_4$	2.2085	g	$Ti[O(CH_2)_3CH_3]_4$	2.2085	g
TPABr	5.72	g	TPABr	7.53	g
NaCl	11.95	g	De-ionized water	60	ml
$Co(NO_3)_2.6H_2O$, VCl_3	x	g	$Co(NO_3)_2.6H_2O$, VCl_3	x	g
$FeCl_3.6H_2O$, $Al(NO_3)_3.9H_2O$			$FeCl_3.6H_2O$, $Al(NO_3)_3.9H_2O$		
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			

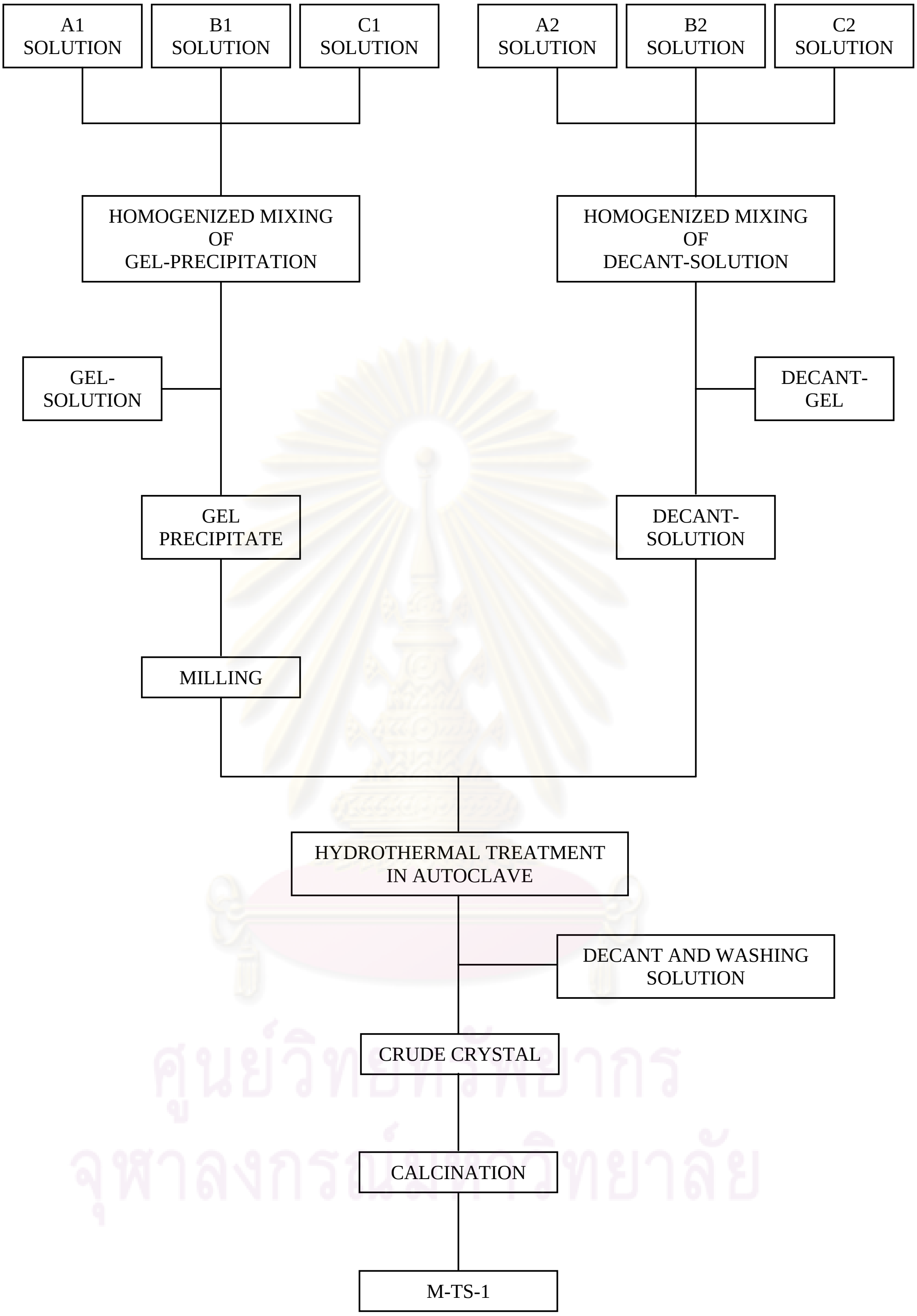


Figure 3.1 The preparation procedure of M-TS-1 by rapid crystallization method.

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, VCl_3 for V, $FeCl_3.6H_2O$ for Fe, $Al(NO_3)_3.9H_2O$ for Al, $Ti[O(CH_2)_3CH_3]_4$ for Ti, and sodium silicate for Si, respectively. TPABr (Tetra-n-propyl ammonium bromide$[(CH_3CH_2CH_2)_4N]Br$) was used as organic template. The atomic ratio of Silicon/Titanium and Silicon/Metal were set at 50, 150, 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 NaOH 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 was replaced by nitrogen gas and pressurized up to 3 kg/cm^2 gauge. Then, the autoclave was heated from room temperature to 160 °C with a heating rate of 2 °C/min, and then heating up to 210 °C with a heating rate of 12 °C/h while being stirred at 60 rpm, followed by cooling the mixture to room temperature in the autoclave overnight. The temperature was programmed under the hydrothermal treatment to minimize the time which was necessary for the crystallization. The product crystals were washed with de-ionized water by centrifugation in order to remove chloride out of the crystals. Then the crystals were dried in an oven at 110 °C for at least 24 h.

3.1.2.3 Calcination

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

M-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 $K\alpha$ radiation with Ni filter. Scans were performed over the 2θ ranges from 6^{o} to 40^{o}.

3.2.4 Fourier transform Infrared (FT-IR)

The functional group on the catalyst surface was determined by FT-IR using Nicolet model Impact 400. 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. The catalyst sample (0.1 g) was treated at 550 °C in helium flow for 1 h and then saturated with 15 %NH_3/He mixture at 80 °C for 15 min. After purging with helium at 100 °C for 1 h to remove weakly physisorbed NH_3, the sample was heated to 550 °C at the rate 10 °C/min in 50 cm^3/min of helium flow. The amount of acid sites on the catalyst surface was calculated from the desorption amount of NH_3. It was determined by measuring the areas of the desorption profiles obtained from the Micromeritics Chemisorb 2750 analyzer.

3.3 Reaction study in hydroxylation of alkyl benzene

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
Ethyl benzene	Analytical	Carlo Erba
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 jointed with glass tube immersing in the mixture of catalyst and hydrogen peroxide in order to allow gaseous alkyl benzene flow through 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 alkyl benzene 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.

3.3.3 Reaction procedure

The hydroxylation of alkyl benzene with hydrogen peroxide was carried out by using a conventional flow shown in Figure 3.2 under the following condition atmospheric pressure.

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

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. Then, the reactor was heated up by raising the oil bath temperature to 70 °C.

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

3) 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.

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

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

6) The next period, the equivalent liquid alkyl benzene was injected into the benzene feed tube again.

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

8) 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.

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

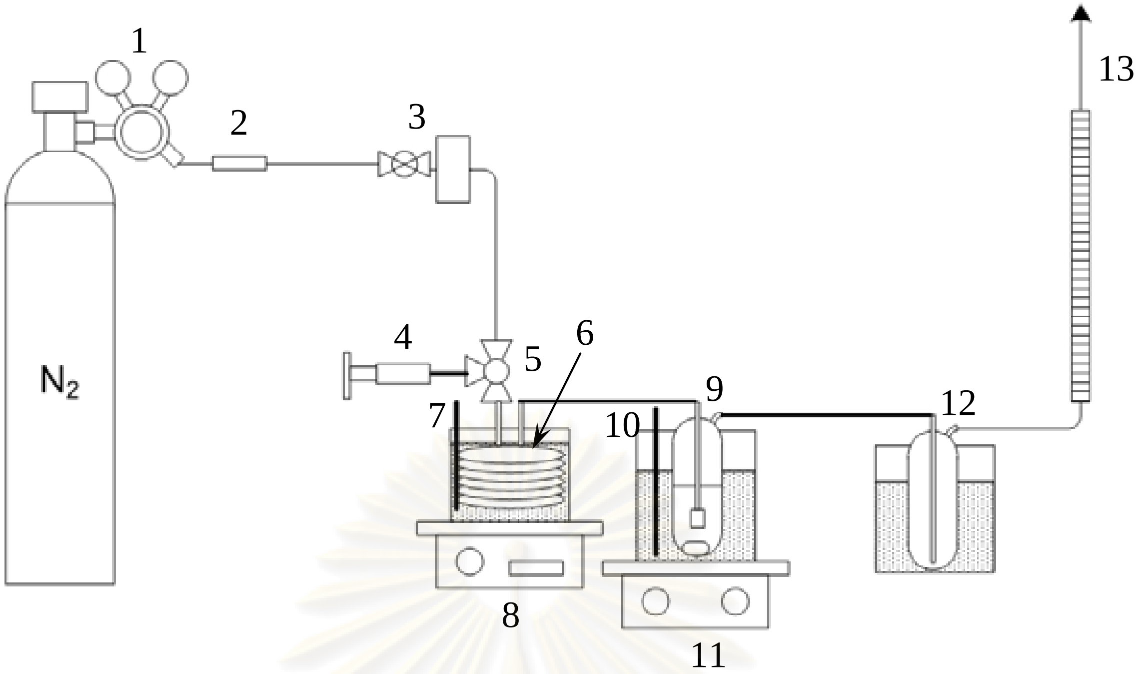


Figure 3.2 Schematic diagram of the reaction apparatus for the hydroxylation of benzene with hydrogen peroxide.

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

3.4 Adsorption of reactants on catalysts

The blank of toluene was prepared for a reference of the adsorption; 0.5 ml reactants as toluene and ethyl benzene, 70 ml ethanol and 40 ml water were added into 100 ml reactor (Scott duran) as showed in Figure 4.3 and stirred. The 0.5 g of TS-1 and M-TS-1 and 40 ml of water were carried out into reactor. The 0.5 g catalyst and 40 ml water were carried out into a reactor and stirred at 90 ºC for 1hr after that cooled down at room temperature. The 0.5 ml of reactant and 70 ml ethanol were added and stir so as to combine phases of toluene and water. When the suppressible solution had deposited, the clear solution, which was a part of toluene non-absorption. It was analyzed by a gas chromatograph equipped with a FID detector (SHIMADZU GC9A). The reactant adsorption on catalyst is determined in Appendix H.

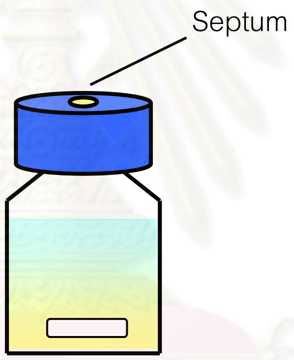


Figure 3.3 The adsorption bottle.

CHAPTER IV

RESULTS AND DISCUSSIONS

The results and discussion in this chapter is divided in two sections: (1) characterization and (2) catalytic hydroxylation of alkyl benzenes. The results from characterization using XRF, XRD, FT-IR, BET and NH_3-TPD are discussed in section 4.1. Finally, the section 4.2 is results of catalytic hydroxylation of alkyl benzenes.

4.1 Catalytic characterization

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

4.1.1 X-ray fluorescence spectroscopy (XRF)

X-Ray Fluorescence Spectrometer (XRF) was used, for the quantitative determination of the M, Ti, and Si contents in the modified TS-1 sample. In Table 4.1, the measured concentrations of the metals M-TS-1 are given. As can be seen the Co, V, Fe, and Al concentrations added in the synthesized procedure were 0.77, 0.51, 2.57 and 0.13, respectively. However, the corporation of each cation (Si, Ti, Al, Co, Fe, and V) into the MFI structure is in random form. Therefore, it is impossible to fix the ratio of Si/Ti and Si/M of the synthesized catalyst for each sample. In addition, the amount of titanium and metal are very low when comparing with the amount of silicon.

Table 4.1 The chemical compositions of the metals and the atomic ratio of Si/Ti and Si/M of samples. (% by mole)

Samples	%Si	%Ti	%M	Si/Ti	Si/M
TS-1	93.92	5.84	none	16.09	none
Al-TS-1	94.11	4.94	0.77	19.04	122.85
Co-TS-1	95.42	3.92	0.51	24.37	186.18
Fe-TS-1	92.26	5.08	2.57	18.15	35.91
V-TS-1	94.46	5.22	0.13	18.08	755.38

4.1.2 X-ray diffraction (XRD)

The crystal of each type of zeolite has different characteristic peaks. Hence, the XRD pattern can be use to identify the structure of zeolite. Figure 4.1 show the XRD patterns of TS-1 and M-TS-1 zeolite. The XRD patterns show six main peaks at 2θ as 8, 8.8, 14.8, 23.1, 24 and 26.7. The pattern obtained is the pattern typical for a crystalline zeolite having a MFI structure (Zhao *et al.*, 2000). The result indicates that the catalyst contained well-defined single-phase and is consistent to those already reported for TS-1 (Taramasso *et al.*, 1983). From Figure 4.1, the XRD patterns from M-TS-1 catalysts have same characteristic peaks as MFI structure the TS-1. Therefore, the incorporation of second metal into TS-1 catalyst does not affect significantly on the MFI structure.

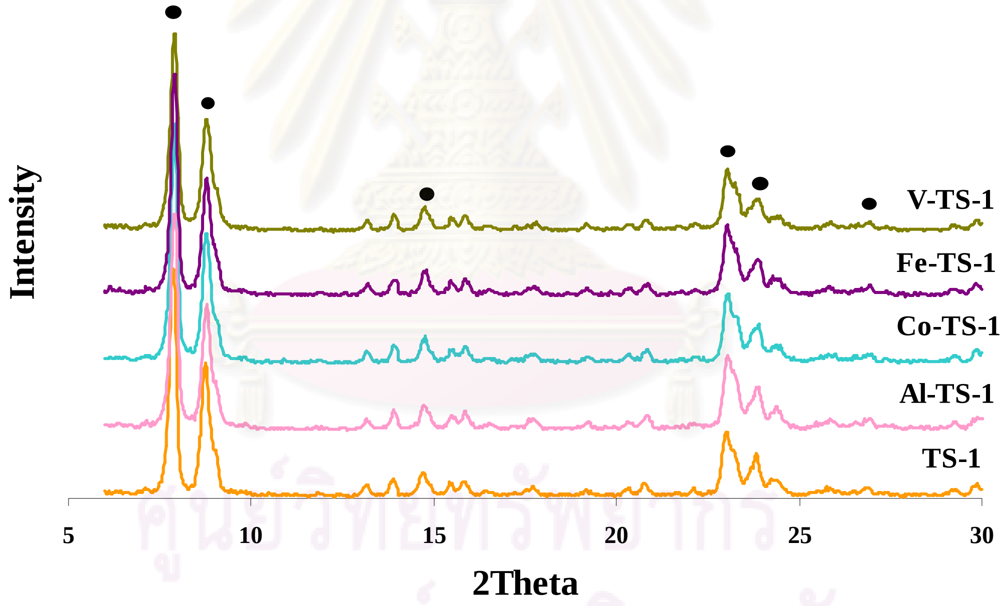


Figure 4.1 XRD patterns of TS-1 and M-TS-1 catalysts.

4.1.3 Fourier-transform infrared spectroscope (FT-IR)

In 2001, Li *et al*. reported that the catalytic performance of TS-1 was related to the amount of Ti in the framework of zeolite with Si/Ti ratio in the gel decreasing, the 960 cm^{-1}band in the FT-IR spectra characterized framework titanium atoms becomes stronger. The strong band at 960 cm^{-1} mean more titanium atoms incorporated into framework. Besides, the research from Pirutko *et al.* (2001) that referred to Zecchina et al. (1991) and Bolis *et al.* (1999) also reported the IR at the position 960 cm^{-1} that is band typical for tetrahedral group $Ti(OSi)_4$ appears in the silicalite spectrum. The IR spectra of the synthesized M-TS-1 and TS-1 catalysts of the present work show the characteristic absorption band of tetrahedral Ti^{4+} in the M-TS-1 and TS-1 framework at 960 cm^{-1} as shown in Figure 4.2.

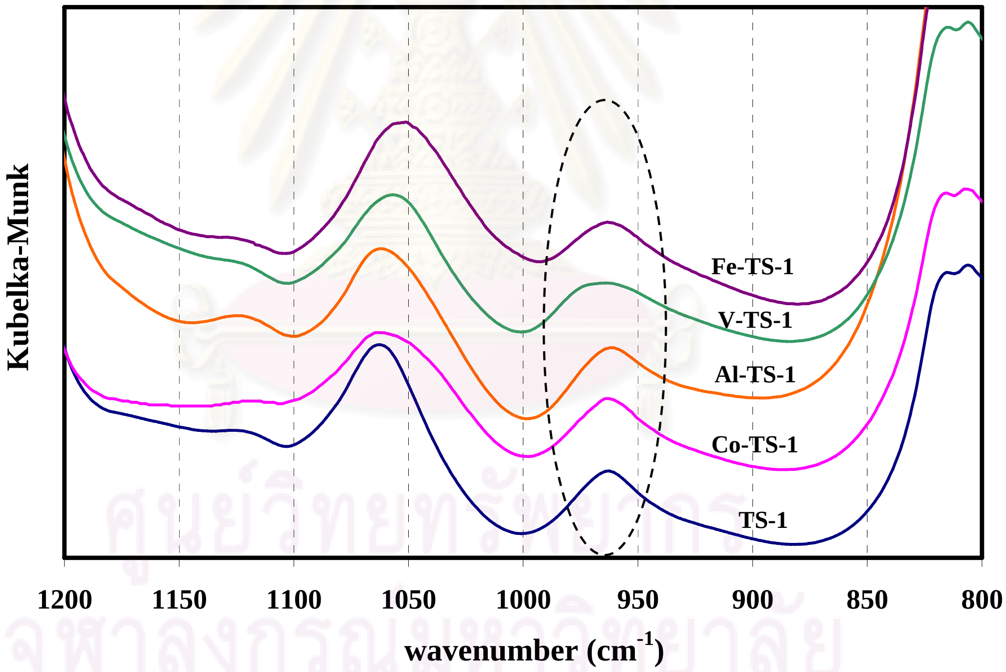


Figure 4.2 IR spectra of TS-1 and M-TS-1 catalysts.

4.1.4 Temperature Programmed Desorption (TPD)

NH_3-TPD was used to determine the strength and amount of the acid site of the catalysts. It is found that each NH_3-TPD profile can be divided into two main peaks. The first peak, will be named here “the weaker acid strength”, appears around 148-160°C and the second peak, will be named here “the stronger acid strength”, appears around 289-352°C as representative in Table 4.2 and Figures 4.3. The peak fitting process, using a freeware programme named “fityk”, was carried out by finding the best fit of skew-Gaussian peak(s) (parameter “splitGaussian” in the programme). The amount of each acid site can be determined from the percentage of each component peak and the total amount of ammonia desorbed. The results which are calculated from the raw data are showed in Appendix F.

Table 4.2 Desorption temperature and acid site quantities of the synthesized TS-1 and M-TS-1 catalysts.

Catalyst	Weaker acid strength		Stronger acid strength		Total acid site (μmol/g)
	Temp. (°C)	Site (μmol/g)	Temp. (°C)	Site (μmol/g)	
TS-1	153	12	313	7	19
Al-TS-1	160	66	352	50	116
Co-TS-1	151	12	-	-	12
Fe-TS-1	150	41	289	43	84
V-TS-1	151	15	-	-	15

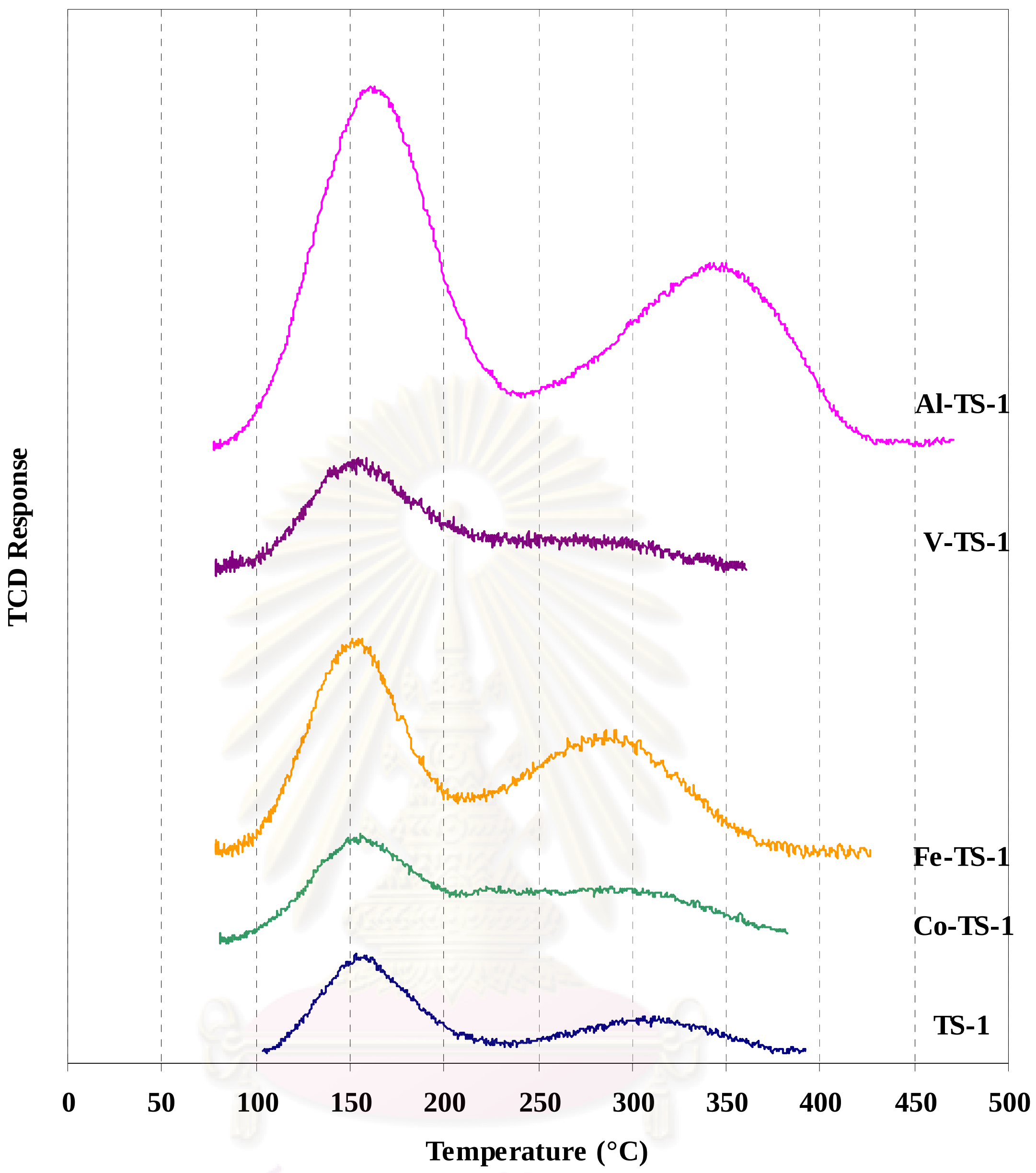


Figure 4.3 NH_3-TPD of TS-1 and M-TS-1 samples.

4.1.5 Brunaur-Emmett (BET surface area), pore volume and pore sized analysis

The surface area, pore volume and pore size of TS-1 and M-TS-1 samples are presented in Table 4.3. The results show that surface area of M-TS-1 increased when the second metal was introduced into TS-1 catalyst. The average pore size shows in the table is the size of meso pore.

Table 4.3 Surface area, pore volume and pore sized of TS-1 and M-TS-1 catalysts.

Sample	A_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
TS-1	350	0.16	28
Al-TS-1	360	0.16	28
Co-TS-1	371	0.16	29
Fe-TS-1	375	0.14	26
V-TS-1	358	0.18	31

4.2 Catalytic hydroxylation of alkyl benzenes

The catalytic reaction of alkyl benzenes (toluene and ethyl benzene) in the bubble reactor over TS-1 and modified TS-1 catalysts are discussed and divided into three sections. The blank run reaction is reported in section 4.2.1. The hydroxylation of toluene reaction is discussed in section 4.2.2 followed by the hydroxylation of ethyl benzene in section 4.2.3.

4.2.1 The blank run reaction

A test of blank run is performed to determine the effect(s) of homogeneous reaction (the direct reaction between the alkyl benzenes (toluene and ethyl benzene) and hydrogen peroxide without any involvement of the catalysts). The experimental procedures are the same as of the normal run but no catalyst is added to the reactor. The analysis of the reaction mixture found no reaction product. Therefore, it can be concluded that any reaction products reported in the subsequent sections come from the reaction with the involvement of the catalysts.

4.2.2 The hydroxylation of toluene

The catalytic activity of toluene hydroxylation over the synthesized catalysts (TS-1 and M-TS-1) with hydrogen peroxide concentrations 30 wt%, 7.5 wt% and 3 wt% in water are summarized in Table 4.4 and showed in Figure 4.4 and Figure 4.5. The volume of hydrogen peroxide solution used in each run is 40 ml which is equal to 388.2 mmol, 97 mmol and 38.8 mmol for the 30 wt%, 7.5 and 3 wt% solutions, respectively. The total amount of toluene used in each run is 1.5 ml (14.1 mmol). 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. Only a small fraction of toluene in the gas bubble can dissolve into the hydrogen peroxide solution due to its very low solubility in water, while the majority of toluene in the bubble leaves the reactor with the 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 The catalytic activity of TS-1 and M-TS-1 catalyst with various concentration of H_2O_2.

Catalysts	wt% H_2O_2	% conversion	% Selectivity		
		Toluene	Benzaldehyde	*o*-cresol	*p*-cresol
TS-1	3	0.15	80.08	19.92	-
	7.5	0.26	86.59	13.41	-
	30	0.32	93.77	6.23	-
Al- TS-1	3	0.80	97.69	2.31	-
	7.5	0.85	96.67	3.33	-
	30	2.40	97.17	1.86	0.97
Co-TS-1	3	0.04	-	100	-
	7.5	0.03	-	100	-
	30	0.19	80.5	13.69	5.82
V-TS-1	3	0.11	67.19	32.81	-
	7.5	0.19	78.74	21.26	-
	30	0.24	91.62	8.38	-

* For Fe-TS-1, due to the severe decomposition reaction of hydrogen peroxide when Fe-TS-1 is added to the hydrogen peroxide solution in the bubble reactor, the hydroxylation reaction using Fe-TS-1 as the catalyst can not be investigated.

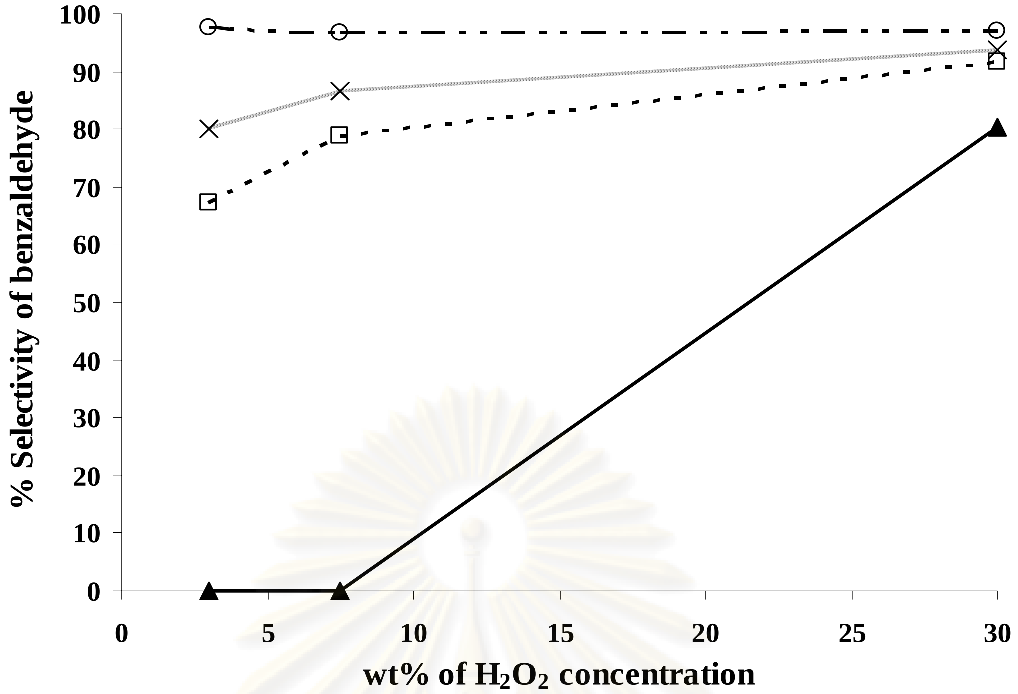


Figure 4.4 Selectivity of benzaldehyde with various concentration of H_2O_2 over TS-1 (╳), Al-TS-1 (○), Co-TS-1 (▲) and V-TS-1 (☐) catalysts.

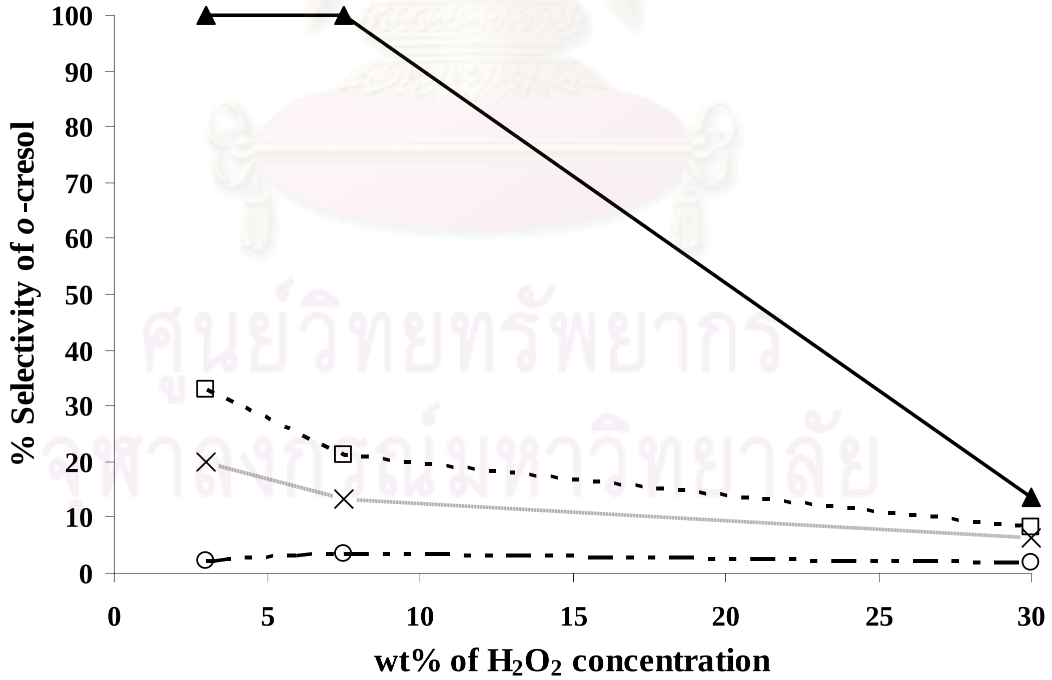


Figure 4.5 Selectivity of *o*-cresol with various concentration of H_2O_2 over TS-1 (╳), Al-TS-1 (○), Co-TS-1 (▲) and V-TS-1 (☐) catalysts.

The data obtained from the hydroxylation of toluene shows that the conversion of toluene increases with the concentration of hydrogen peroxide, but not in a proportional ratio. For example, when the concentration of H_2O_2 is decreased from 30wt% to 3 wt% (10 times decrease), the conversion of toluene drops from 0.32% to 0.15% (approximately 2 times) for TS-1, from 2.4% to 0.8% (approximately 3 times) for Al-TS-1, from 0.19% to 0.04% (approximately 5 times) for Co-TS-1, and from 0.24% to 0.11% (approximately 2 times) for V-TS-1. The main reaction products of toluene hydroxylation over TS-1, Al-TS-1 and V-TS-1 are benzaldehyde and *o*-cresol at every H_2O_2 concentration. In addition, the observed selectivities of benzaldehyde are much higher than that of *o*-cresol. Co-TS-1 behaves differently from the other catalysts. At low H_2O_2 concentrations (3 wt% and 7.5 wt%), *o*-cresol is the only reaction product formed. When the concentration of H_2O_2 is raised to 30wt%, benzaldehyde and *p*-cresol are found in the reaction mixture. It should be noted here that only in the cases of Al-TS-1 and Co-TS-1 at high concentration of hydrogen peroxide (30 wt%), *p*-cresol is also formed in a significant amount. In summary, the conversion of toluene over the synthesized catalysts can be arranged in the following order: Al-TS-1 > TS-1 > V-TS-1 > Co-TS-1.

Kumar and co-workers (Kumar and Bhaumik (1998) and Kumar et al. (1999)) reported that *p*-isomer is the major product in tri-phase reaction and *o*-isomer is the major product in bi-phase. They explained that under the tri-phase condition, the reaction occurred mainly inside “the channels” of TS-1 on the basis of restricted 10-ring pore opening, whereas under the bi-phase condition the active sites presented on “the surface” were responsible for reaction.

The data obtained from the XRD and BET analysis presents that the synthesized catalysts of the present work have both micro pore system (“the channels” in the works of Kumar and co-workers mentioned in the previous paragraph) and meso pore system (“the surface” in the works of Kumar and co-workers mentioned above). The data showed in Table 4.4 and the information presented above show that the concentration of hydrogen peroxide affects the formation of *p*-cresol, especially in the case of Al-TS-1 and Co-TS-1. This phenomenon can be explained in a similar way as of the work of Kumar and co-workers.

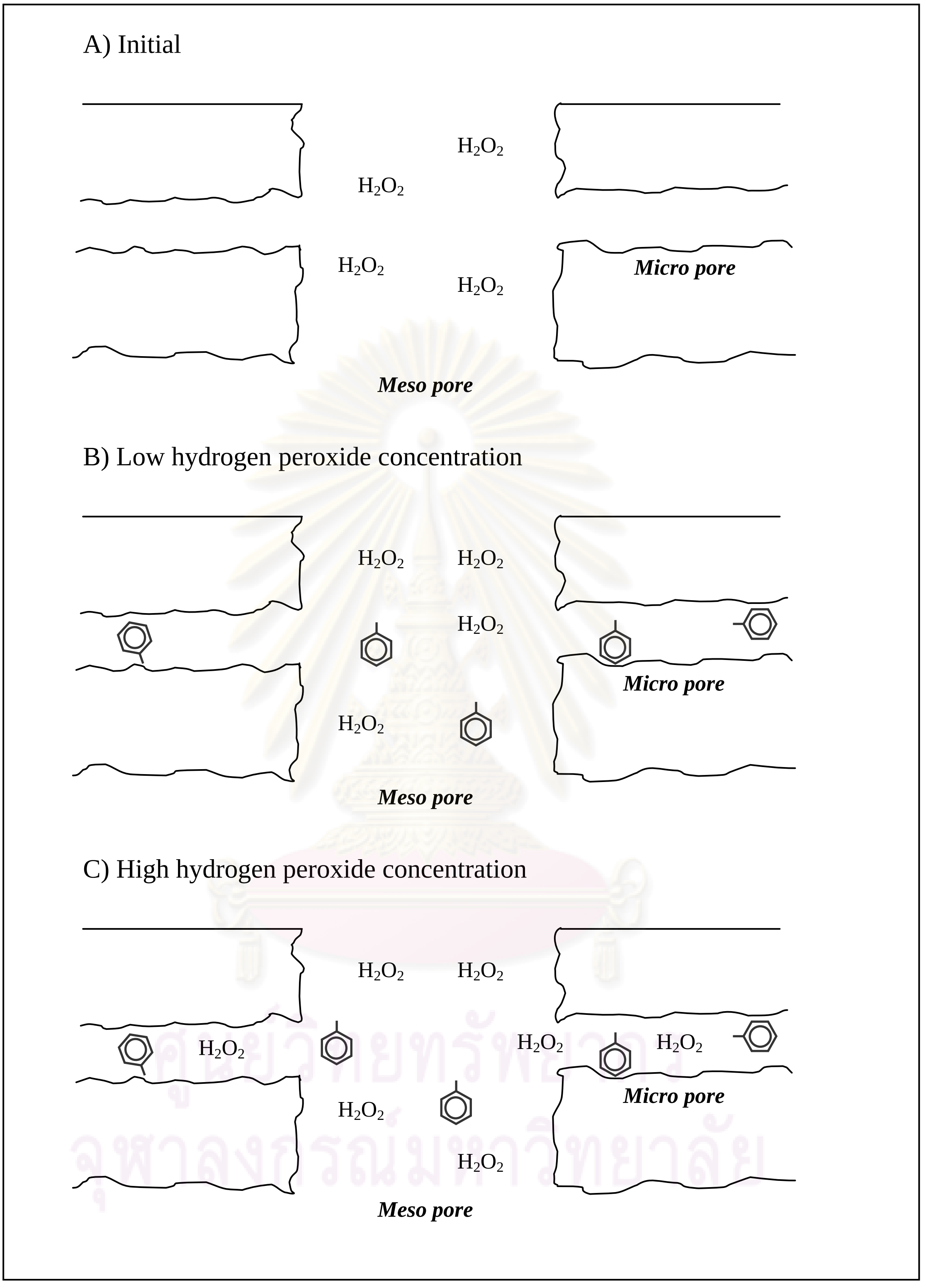
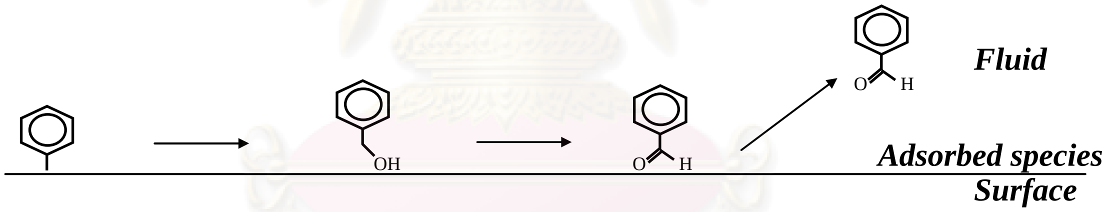
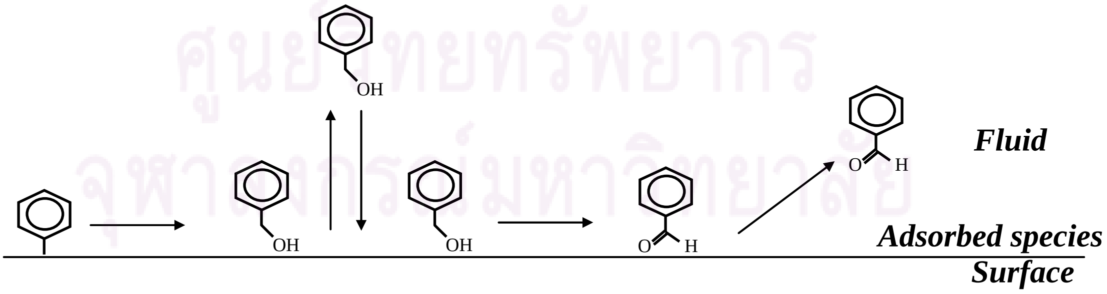


Figure 4.6 Schematic diagram of competitive adsorption between H_2O_2 and toluene at difference H_2O_2 concentration.

Before the gas bubble (with dissolved toluene) is fed to the reactor, the pores of the catalyst in the reactor are filled with H_2O_2 solution. When the gas bubble is fed to the reactor, toluene begins to present in the liquid phase. The concentration of toluene in the liquid phase, though, much lower than the concentration of H_2O_2 peroxide, toluene can replace the H_2O_2 solution previously filled the catalyst pores (both micro and meso pore systems) due to the nature of the catalyst that prefer the adsorption of a non-polar molecule. Therefore, at low a hydrogen peroxide concentration, hydrogen peroxide can competitively adsorb with toluene only in the meso pore system. This phenomenon is illustrated schematically in Figure 4.6. The consequent is the reaction between adsorbed hydrogen peroxide and toluene in the meso pore system which leads to the formation of *o*-cresol and benzaldehyde. At high hydrogen peroxide concentration, some part of hydrogen peroxide molecule can penetrate into the micro pore system due to the higher driving force (concentration difference between the outside and the inside). This leads to the observed formation of *p*-cresol when the concentration of hydrogen peroxide is raised to 30wt%.



Scheme 1



Scheme 2

Figure 4.7 Schematic diagram of mechanism of toluene oxidation on catalyst.

The higher amount of benzaldehyde formed is likely due to the more active of the methyl group than the benzene ring. Theoretically, the oxidation of toluene to benzaldehyde should form benzyl alcohol, a primary alcohol ($C_6H_5CH_2$-OH), first. There are two possible explanations to explain the non-appearance of benzyl alcohol in the product mixture. The first one is the direct oxidation of toluene to benzaldehyde without desorption of any intermediate(s) formed (scheme 1 in Figure 4.7). The second one is the fast oxidation of benzyl alcohol (if really formed) to benzaldehyde (scheme 2 in Figure 4.7). In our case, the first explanation is preferred. This is because if the formation of benzaldehyde follows the second explanation, trace of benzyl alcohol should be observed in the reaction products.

4.2.2.1 Mechanism for oxidation of toluene

Another possible mechanism for the formation of benzaldehyde is shown in Figure 4.8 below. The mechanism in Figure 4.8 follows the generally accepted free radical substitution of halogen. The only difference is halogen atom (X•) is replaced by hydroxyl free radical (•OH). The initiating step is the breaking of O-O bond of the hydrogen peroxide into two hydroxyl free radicals (step 1 in Figure 4.8). The oxygen atom of the hydroxyl free radical is very reactive because it has an incomplete valance shell. When the hydroxyl free radical collides with the methyl group of toluene molecule, it will abstract a hydrogen atom from the methyl group with results in the formation of benzyl alcohol. Due to the nature of primary alcohol which can be easily oxidized, the benzyl alcohol forms is then rapidly oxidized by hydrogen peroxide to benzaldehyde (step 2 in Figure 4.8)

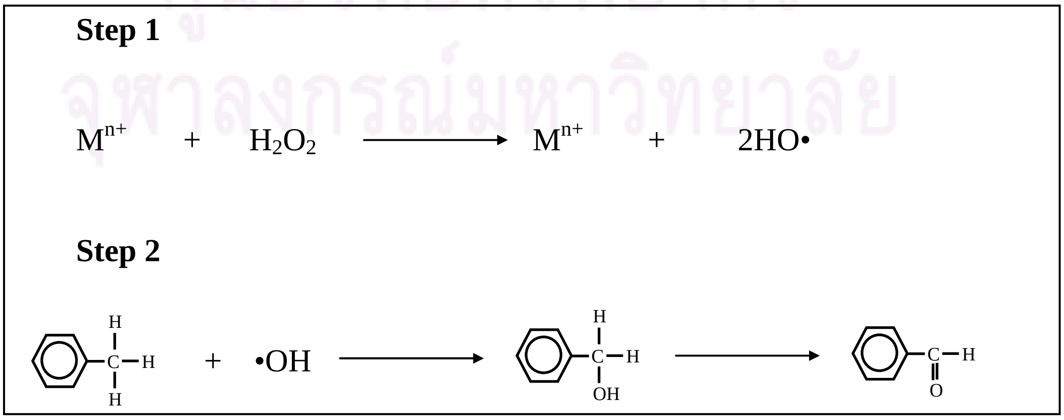
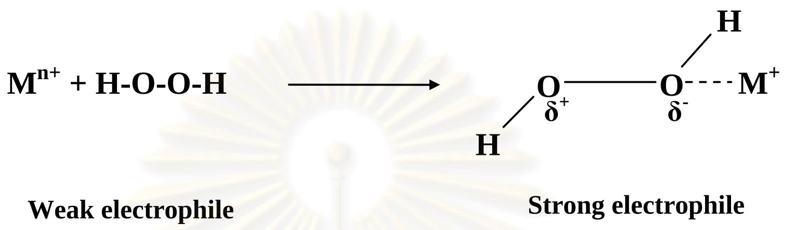


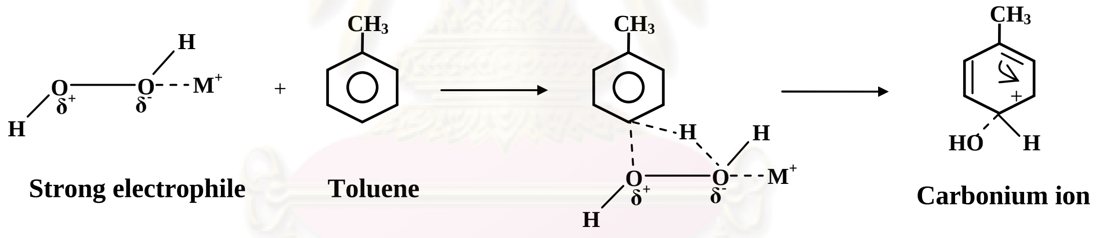
Figure 4.8 The mechanism of benzaldehyde formation by hydroxyl free radical.

In the present study, it is believed that the mechanism of toluene hydroxylation follows the generally recognized electrophilic aromatic substitution on benzene ring. Therefore, the following mechanism of the hydroxylation of toluene over TS-1 and M-TS-1 is proposed. This path of electrophilic aromatic substitution to form ring oxidation products of toluene hydroxylation

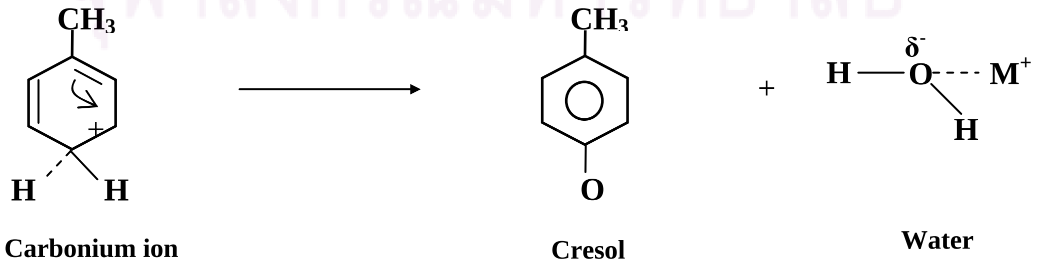
Step 1: Metal cations act as Lewis acid that convert H_2O_2 to the more reactive electrophile.



Step 2: The formed reactive electrophile attacks the ring at ortho or para positions, resulting in the formation of cabonium ion.



Step 3: The intermediate carbonium ion can eliminate a proton, giving an overall result of substitution.



4.2.2.2 The roles of second metal

Since, catalytic activity and selectivity depend on the amount of active site, metal cation, the amount of active sites should be taken into consideration along with conversion and selectivity. Due to the amount of titanium and second metal in each synthesized catalysts is not equal, the conversion per of active site (Ti + M) will be used for catalytic activity comparison as shown in Table 4.5 and Table 4.6.

Table 4.5 Toluene conversion and toluene conversion per mole of total metal on TS-1 and M-TS-1 at 3, 7.5 and 30 wt% hydrogen peroxide concentration.

Catalysts	%Ti	%M	%Conversion			%Conversion per mole of (Ti + M)		
			3 wt% H_2O_2	7.5 wt% H_2O_2	30 wt% H_2O_2	3 wt% H_2O_2	7.5 wt% H_2O_2	30 wt% H_2O_2
TS-1	5.84	none	0.15	0.26	0.32	161.68	269.45	332.59
Al-TS-1	4.94	0.77	0.80	0.85	2.41	756.97	807.17	2277.36
Co-TS-1	3.92	0.51	0.04	0.03	0.19	56.58	47.16	262.28
V-TS-1	5.22	0.13	0.11	0.19	0.25	127.33	215.11	274.9

Table 4.6 Selectivity and mole of *o*-cresol on TS-1 and M-TS-1 at 3, 7.5 and 30 wt% hydrogen peroxide concentration.

Catalyst	%selectivity of *o*-cresol			mole of *o*-cresol		
	3 wt% H_2O_2	7.50 wt% H_2O_2	30 wt% H_2O_2	3 wt% H_2O_2	7.50 wt% H_2O_2	30 wt% H_2O_2
TS-1	19.92	13.41	6.23	2.78E-10	3.11E-10	1.79E-10
Al-TS-1	2.31	3.33	1.86	1.67E-10	2.56E-10	4.03E-10
Co-TS-1	100	100	13.69	3.71E-10	3.10E-10	2.36E-10
V-TS-1	32.81	21.26	8.38	3.37E-10	3.69E-10	1.86E-10

The results in Table 4.5 - 4.6 above show that changing of metal amount of TS-1 and M-TS-1 has effect on the conversion of toluene, but not in proportional ratio when compare with TS-1. For example, Co-TS-1 and V-TS-1 have 0.67 and 0.89 times, respectively, lesser amount of Ti when compare with TS-l but their conversion at 3 wt% H_2O_2 decrease from 0.15% to 0.04% (approximately 4 times) for Co-TS-1 and from 0.15% to 0.11% (approximately 1.36 times) for V-TS-1, respectively. On the contrary, the selectivity to cresol of Co-TS-1 and V-TS-1 increases when the second metal is incorporated. These results point that the second metal inhibits the formation of side chain oxidation (benzaldehyde). In addition, the observed higher amount of cresol formed suggests that the second metal also enhances the formation of ring oxidation product (cresol). Especially, Co-TS-1 gives a hundred percent of *o*-cresol selectivity.

Al cation behaves differently from Co and V cations. Amount of total metal (titanium and second metal) of Al-TS-1 and TS-1 is equal but the conversion on Al-TS-1 is greater than TS-1. Table 4.6 shows that at high H_2O_2 concentration (30 wt%) the Al cation promotes both the formation of ring oxidation products (*o*-cresol and *p*-cresol) and side chain oxidation product (benzaldehyde). In the case of low H_2O_2 concentration found less amount of *o*-cresol whereas benzaldehyde was selected to produce in a large amount.

4.2.3 The hydroxylation of ethyl benzene

The catalytic activity of ethyl benzene over synthesized catalysts (TS-1, Al-TS-1, Co-TS-1 and V-TS-1) using 3 wt% of hydrogen peroxide concentration, the condition that give highest selectivity of oxidation ring in toluene hydroxylation, found acetophenone and 1-phenyl ethanol that are side chain oxidation products as shown in Figure 4.9. The products were found in trace amount due to lower solubility of ethyl benzene in water when compared with toluene (the solubility of toluene and ethyl benzene is 0.053 g/100 ml and 0.015 g/100 ml, respectively) which leads to a fewer amount of ethyl benzene on catalyst surface as shown in adsorption graph (Figure 4.10).

At high hydrogen peroxide concentration (7.5 and 30 wt%) still found products in trace amount. In addition, some catalysts accelerate hydrogen peroxide decomposition so severe that the hydroxylation reaction cannot be carried out. In the present work, we have interested in the substitution at aromatic ring that give the ring oxidation products. Therefore, the hydroxylation of ethyl benzene will be not further investigated.

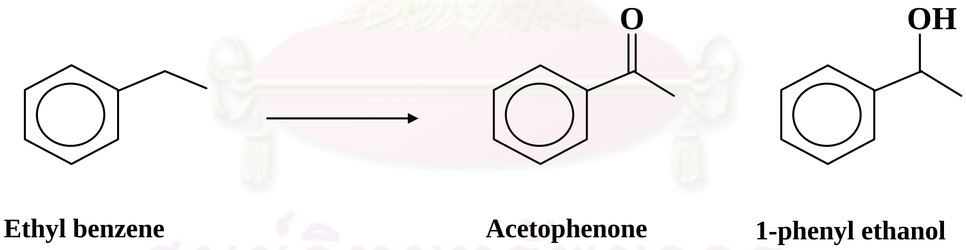


Figure 4.9 The hydroxylation of ethyl benzene.

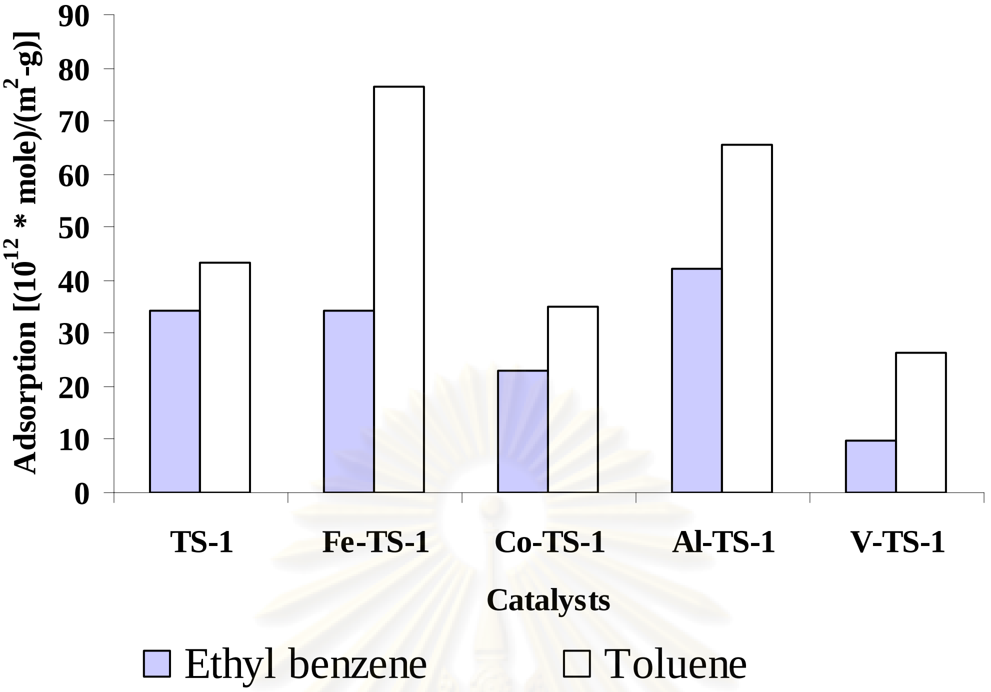


Figure 4.10 The adsorption of toluene and ethyl benzene on surface of TS-1 and M-TS-1 catalyst.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

In present work, the hydroxylation of alkyl benzenes in a bubble reactor over TS-1 and modified TS-1 (Al-TS-1, Co-TS-1, Fe-TS-1 and V-TS-1) catalysts using 3, 7.5 and 30 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. Acetophenone and 1-phenyl ethanol are side chain oxidation products that are observed from hydroxylation of ethyl benzene.

2. The synthesized catalysts (TS-1 and M-TS-1) have meso pore and micro pore. The *o*-cresol and benzaldehyde product are produced in meso pore system whereas *p*-cresol are formed in micro pore system.

3. The possible mechanism of benzaldehyde formation is substitution by hydroxyl free radical at methyl group to form benzyl alcohol that is rapidly oxidized to benzaldehyde product by hydrogen peroxide.

4. The cresol product from toluene hydroxylation is believed that is performed by electrophilic aromatic substitution over TS-1 and M-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.

5. Co and V ion on catalyst enhance the formation of aromatic ring oxidation (cresol) and inhibit the production of the side chain oxidation product (benzaldehyde). Especially, Co-TS-1 gives a hundred percent selectivity of o-cresol product.

6. In the case of Al-TS-1, at high hydrogen peroxide concentration (30 wt%) Al ion promotes the oxidation at aromatic ring and inhibit the formation of the ring oxidation product at low hydrogen peroxide concentration (3 and 7.5 wt%).

7. The products from hydroxylation of ethyl benzene are found in trace amount due to low solubility in water which leads to a fewer amount of ethyl benzene on catalyst surface.

5.2 Recommendations

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

1. Since in some catalysts enhance the production benzaldehyde (side chain oxidation) when the high concentration of hydrogen peroxide was placed in reactor in liquid phase, therefore the feeding procedure of hydrogen peroxide in gas phase using packed bed reactor should be tried.

2. Owing to the at low concentration hydrogen peroxide Co-TS-1 and V-TS-1 give high selectivity of ring oxidation. Especially, the Co-TS-1 hundred percent selectivity of ring oxidation, therefore The Co-TS-1 and V-TS-1 should be further investigated in electrophilic aromatic substitution reaction.

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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.

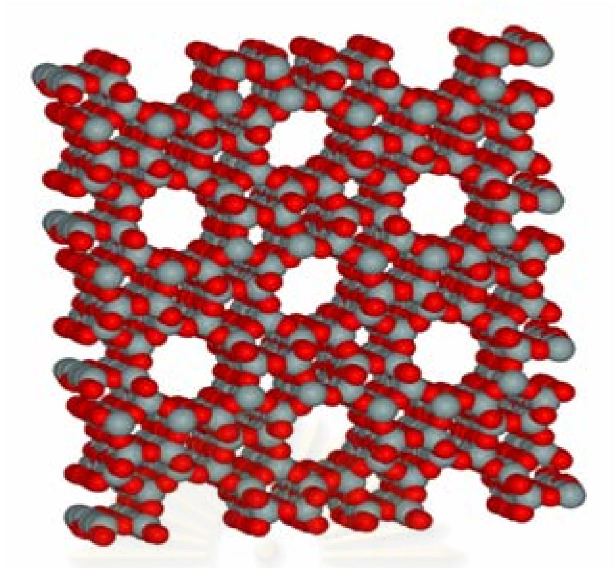


Figure A1 The micro porous molecular structure of a zeolite, ZSM-5. (en.wikipedia.org/wiki/Zeolite)

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.

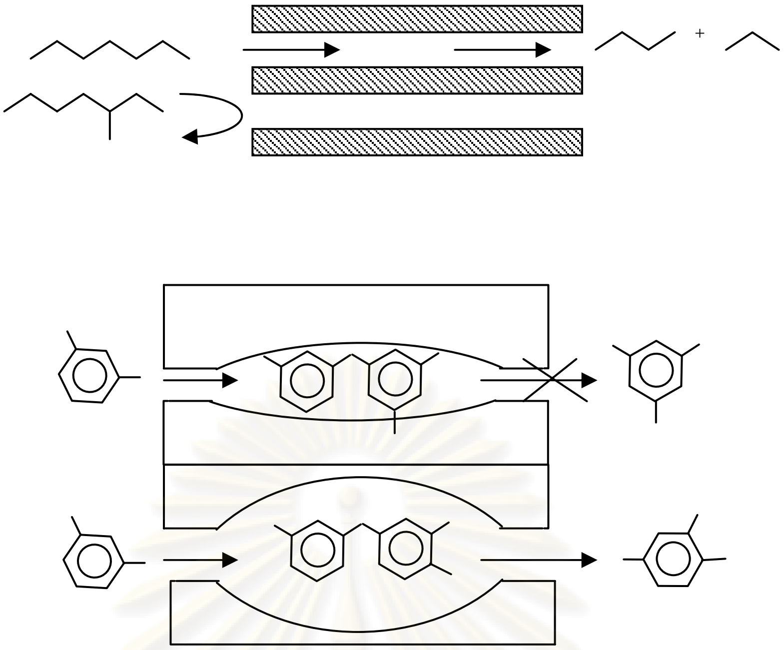


Figure A2 Diagram of shape selectivity on zeolite.

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 TS-1and M-TS-1 catalyst.

Catalysts	wt% H_2O_2	% conversion Toluene	% Selectivity			Mole of products		
			Benzaldehyde	*o*-cresol	*p*-cresol	Benzaldehyde	*o*-cresol	*p*-cresol
TS-1	3	0.15	80.08	19.92	-	1.12E-09	2.78E-10	-
	7.5	0.26	86.59	13.41	-	2.01E-09	3.11E-10	-
	30	0.32	93.77	6.23	-	2.69E-09	1.79E-10	-
Al- TS-1	3	0.8	97.69	2.31	-	7.05E-09	1.67E-10	-
	7.5	0.85	96.67	3.33	-	7.44E-09	2.56E-10	-
	30	2.4	97.17	1.86	0.97	2.11E-08	4.03E-10	2.11E-10
Co-TS-1	3	0.04	-	100	-	-	3.71E-10	-
	7.5	0.03	-	100	-	-	3.10E-10	-
	30	0.19	80.5	13.69	5.82	1.39E-09	2.36E-10	1.00E-10
V-TS-1	3	0.11	67.19	32.81	-	6.91E-10	3.37E-10	-
	7.5	0.19	78.74	21.26	-	1.37E-09	3.69E-10	-
	30	0.24	91.62	8.38	-	2.03E-09	1.86E-10	-

APPENDIX C

CALIBRATION CURVES

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

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 and ethyl benzene are illustrated in Figure C1-C5, respectively.

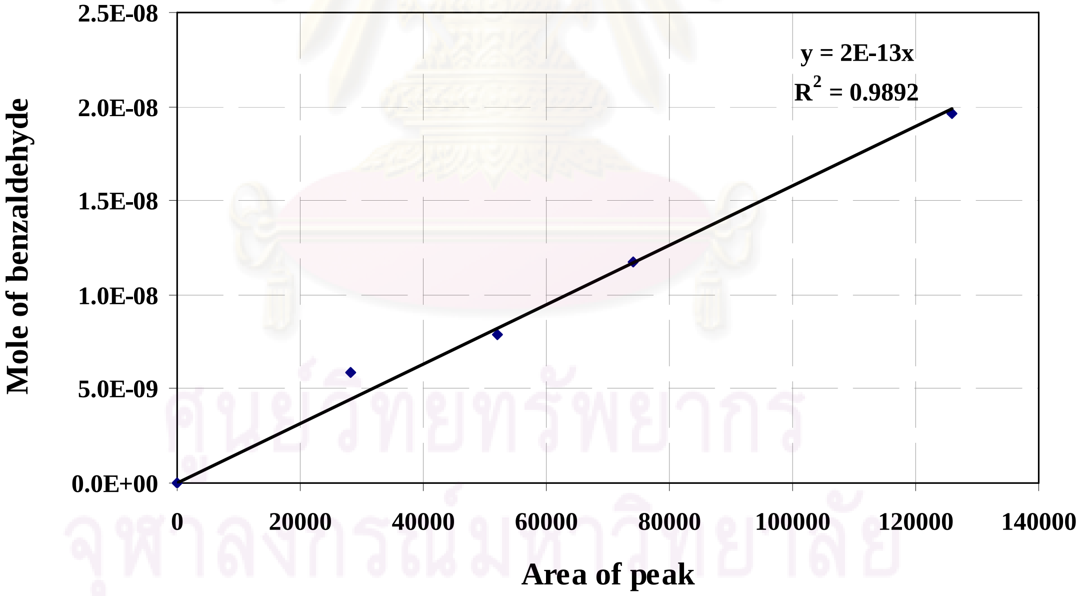


Figure C1 The calibration curve of benzaldehyde.

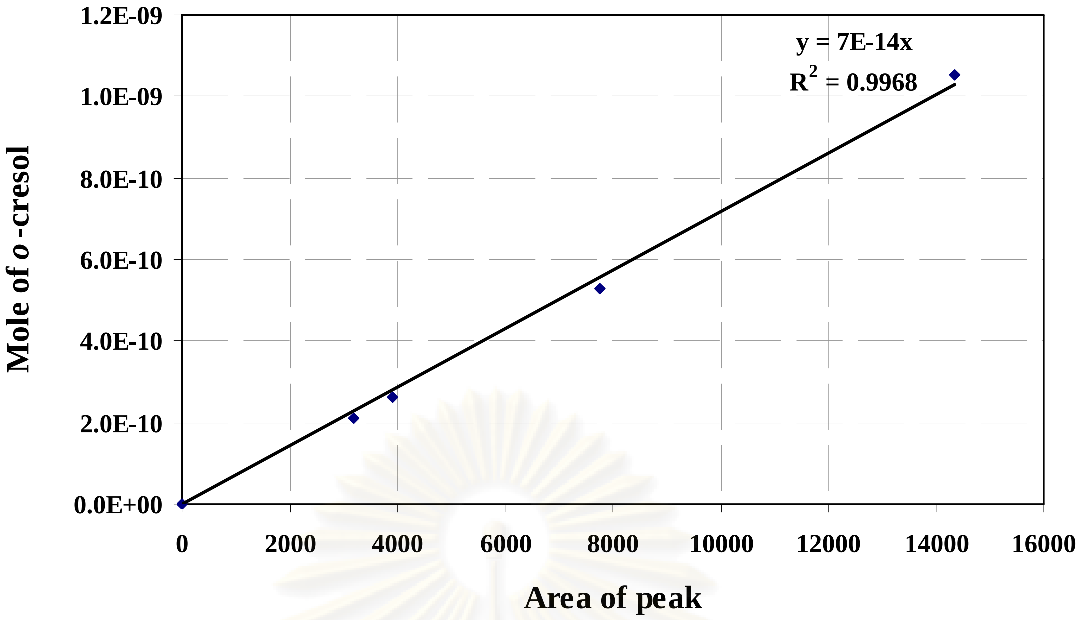


Figure C2 The calibration curve of *o*-cresol.

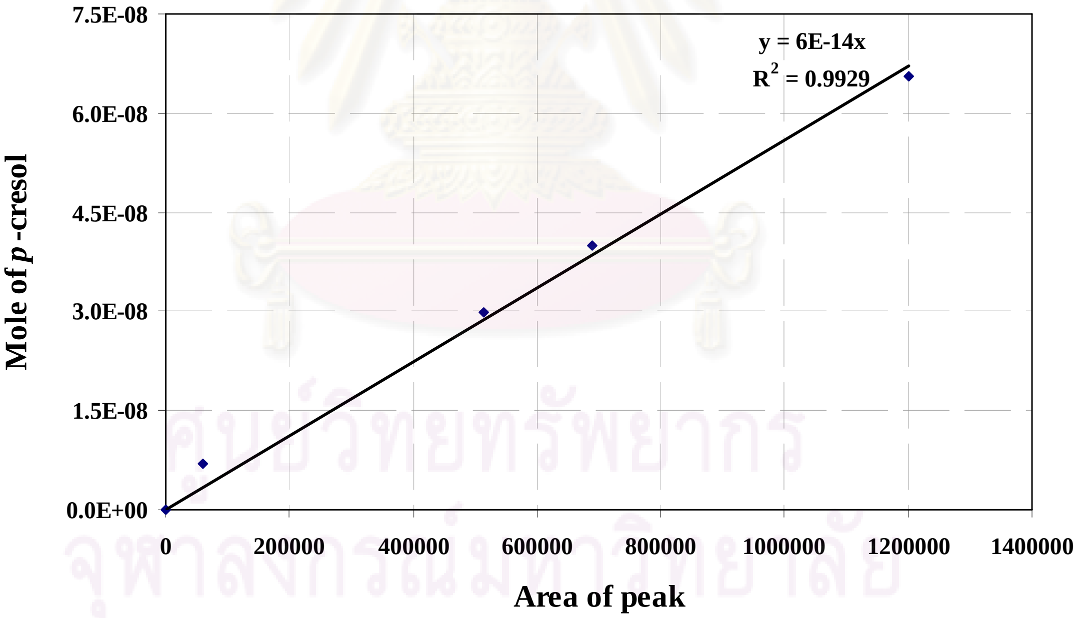


Figure C3 The calibration curve of *p*-cresol.

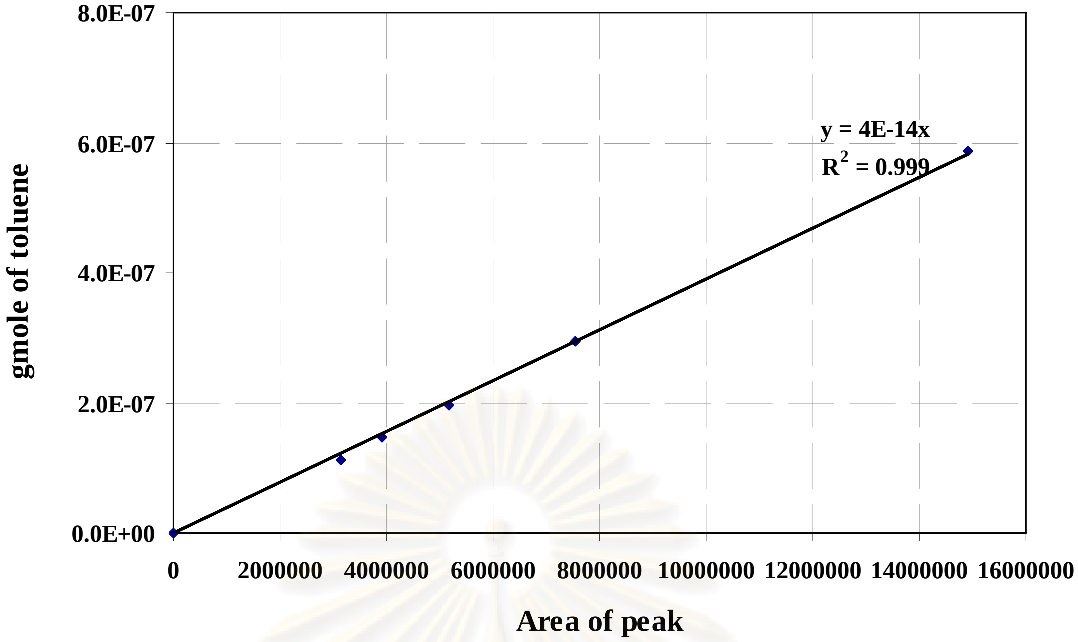


Figure C4 The calibration curve of toluene.

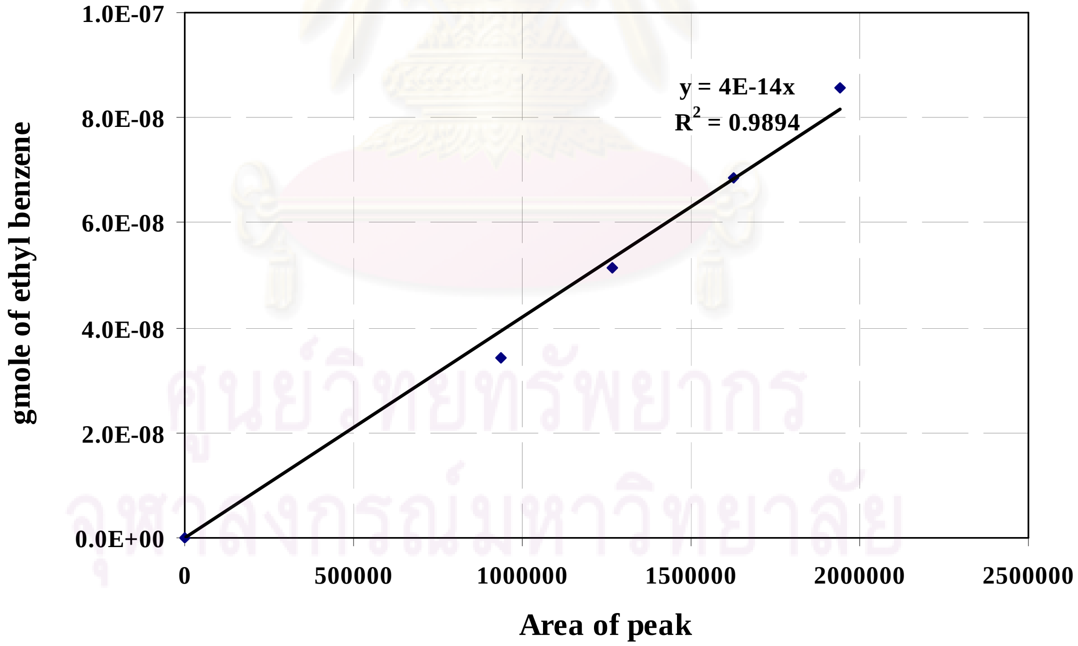


Figure C5 The calibration curve of ethyl benzene.

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 toluene hydroxylation

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

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

Overall mole of *o*-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.,

$$\text{Mole of } o\text{-cresol} = ((\text{area of } o\text{-cresol peak from integrator plot on GC-9A}) \times 7.0\times10^{-14}) \qquad \text{(D3)}$$

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

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:

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

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

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

= 6.546×10^{-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 = 30

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

Table F1 Reported total peak area from Micromeritrics Chemisorb 2750.

Sample	Report total peak area
TS-1	0.007694
Al-TS-1	0.049063
Co-TS-1	0.013191
Fe-TS-1	0.034511
V-TS-1	0.010188

Calulation of total acid sites

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

1. Conversion of total peak area to peak volume

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

$$\begin{aligned} \text{Total peak volume} &= 77.5016 \times \text{total peak area} \\ &= 77.5016 \times 0.007694 \\ &= 0.5963 \text{ ml} \end{aligned}$$

2. Calculation for adsorbed volume of 15% NH_3

$$\begin{aligned}\text{adsorbed volume of 15\% NH}_3 &= 0.15 \times \text{total peak volume}\\ &= 0.15 \times 0.5963\ \text{ml}\\ &= 0.0894\ \text{ml}\end{aligned}$$

3. Total acid sties are calculated from the following equation

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

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

$$\text{Total acid sites} = \frac{0.0894\ \text{ml} \times 101.325\ \text{Pa}}{\left(8.314 \times 10^{-3}\ \frac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}}\right) \times 298\ \text{K} \times (0.1948\ \text{g})}$$

$$= 18.78\ \mu\text{mol H}^+/\text{g}$$

Calculation of acid site ratio

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

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

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

From Figure F6., 1^{st} peak area and 2^{nd} peak area are equal to 0.0162 and 0.0084, respectively.

$$\text{The ratio of weak acid} = \frac{0.0162}{0.0162 + 0.0084} \times 100\ \%$$

$$= 65.96\ \%$$

$$\text{therefore, the ratio of strong acid} = 100 - 65.96\ \%$$

$$= 34.04\ \%$$

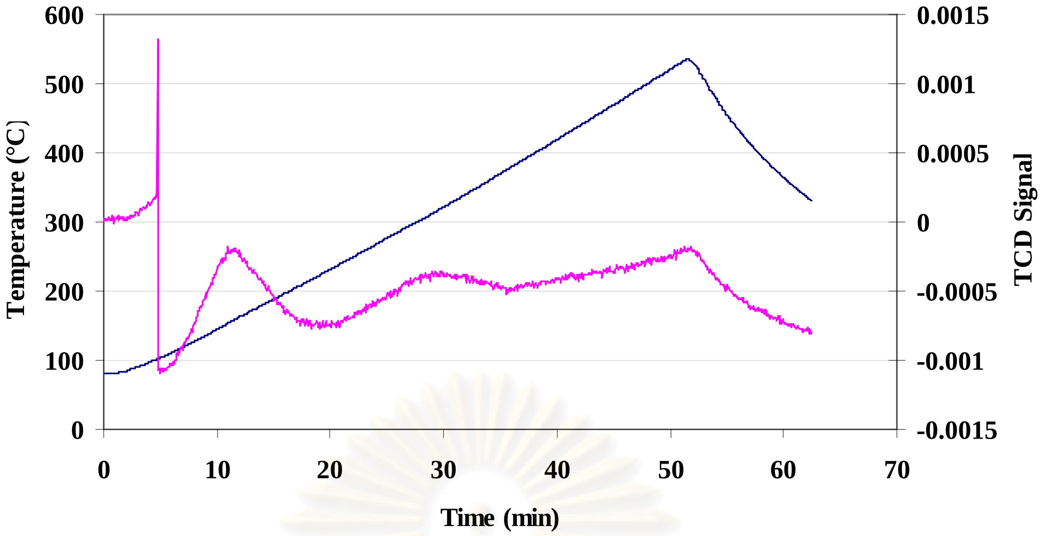


Figure F1 TCD signal and temperature versus time of TS-1 from Micromeritrics Chemisorb 2750.

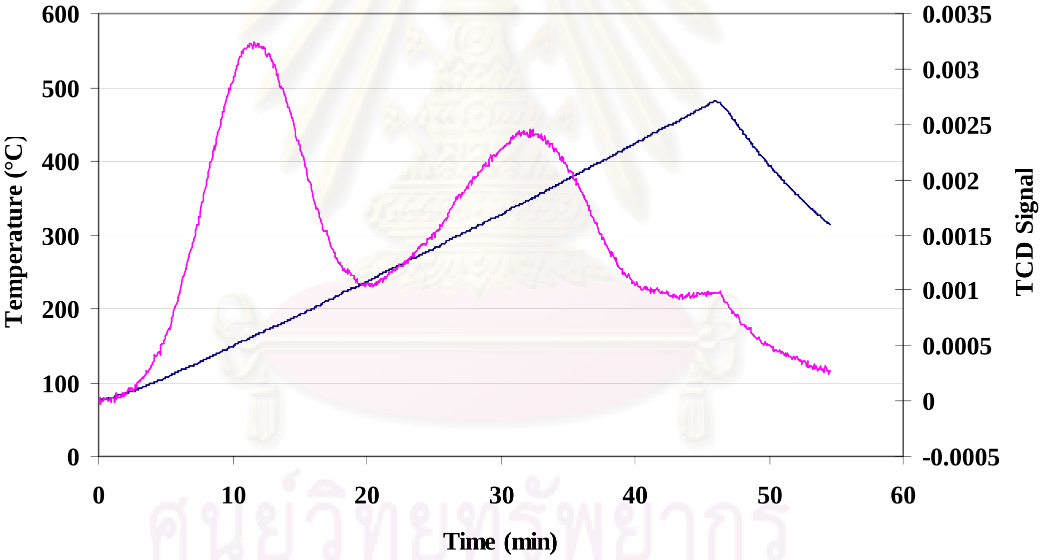


Figure F2 TCD signal and temperature versus time of Al-TS-1 from Micromeritrics Chemisorb 2750.

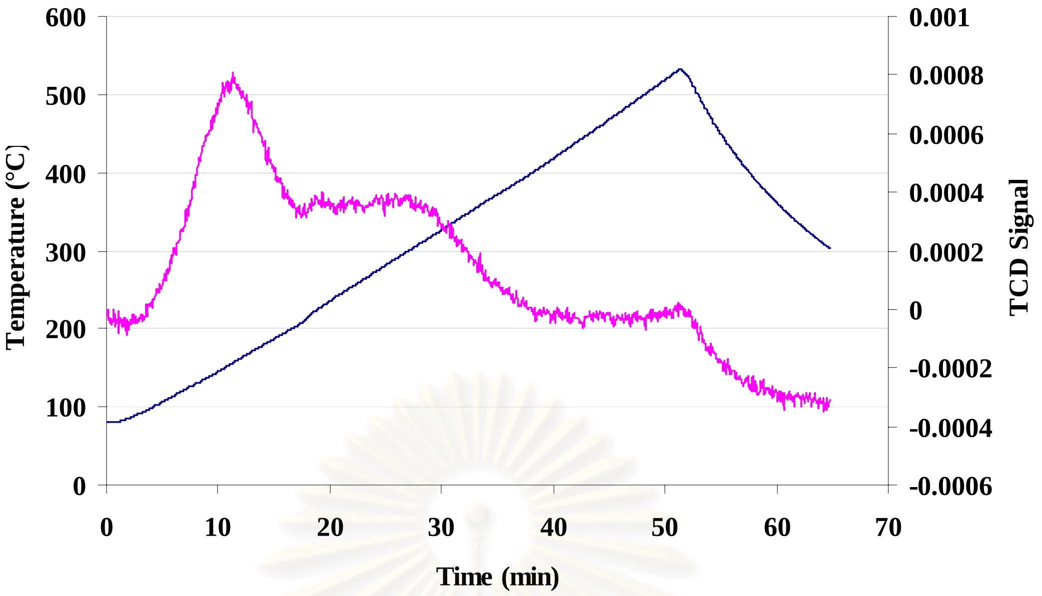


Figure F3 TCD signal and temperature versus time of Co-TS-1 from Micromeritrics Chemisorb 2750.

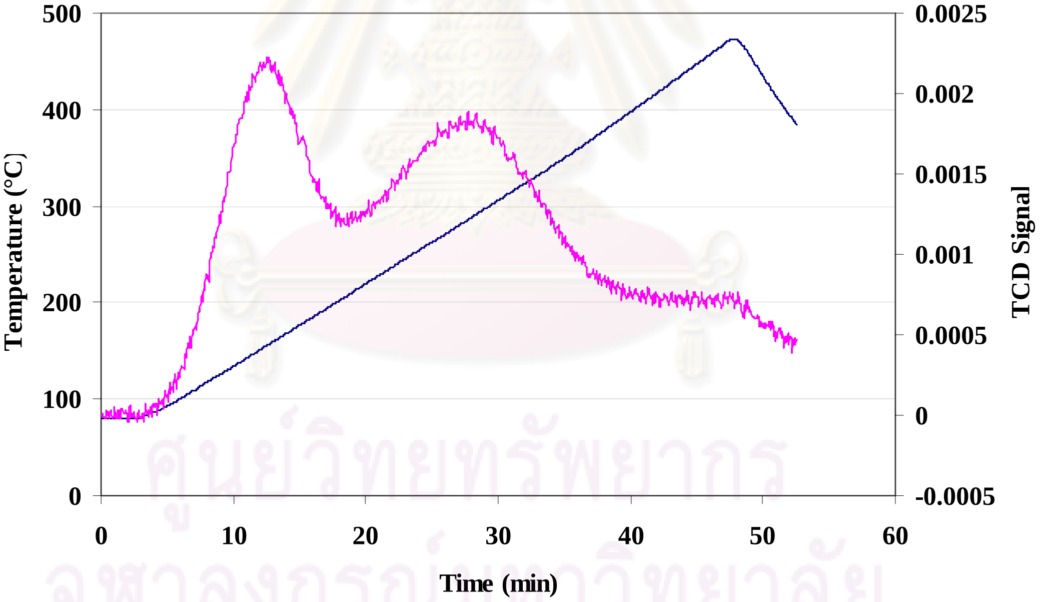


Figure F4 TCD signal and temperature versus time of Fe-TS-1 from Micromeritrics Chemisorb 2750.

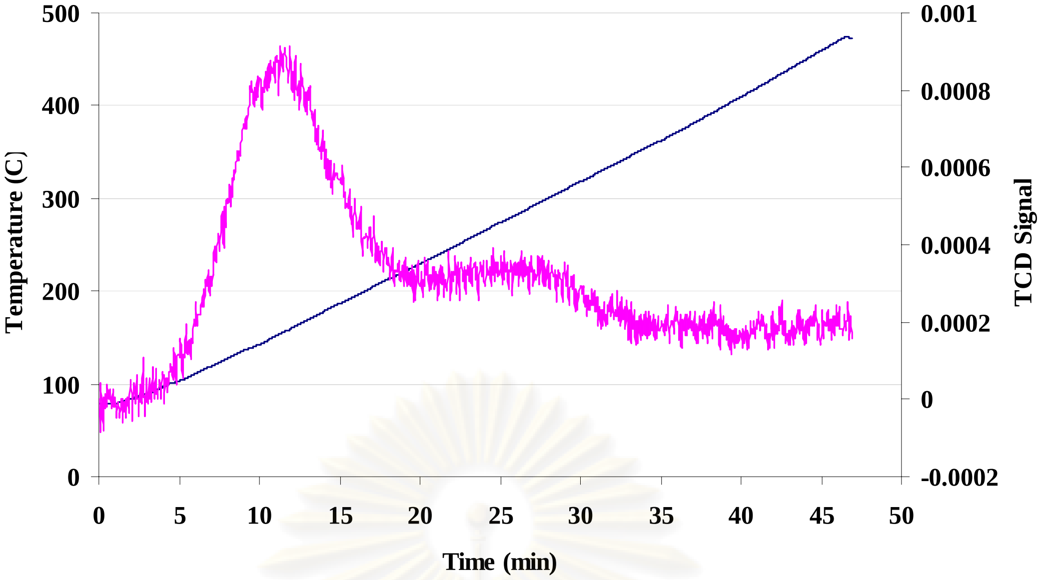
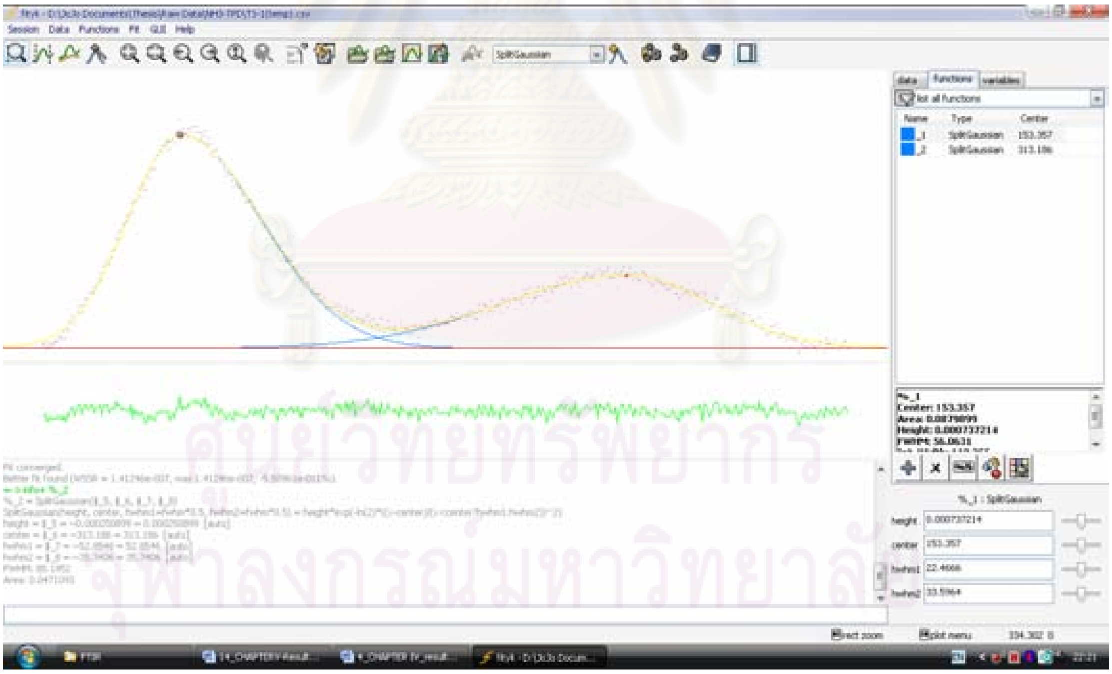


Figure F5 TCD signal and temperature versus time of V-TS-1 from Micromeritrics Chemisorb 2750.

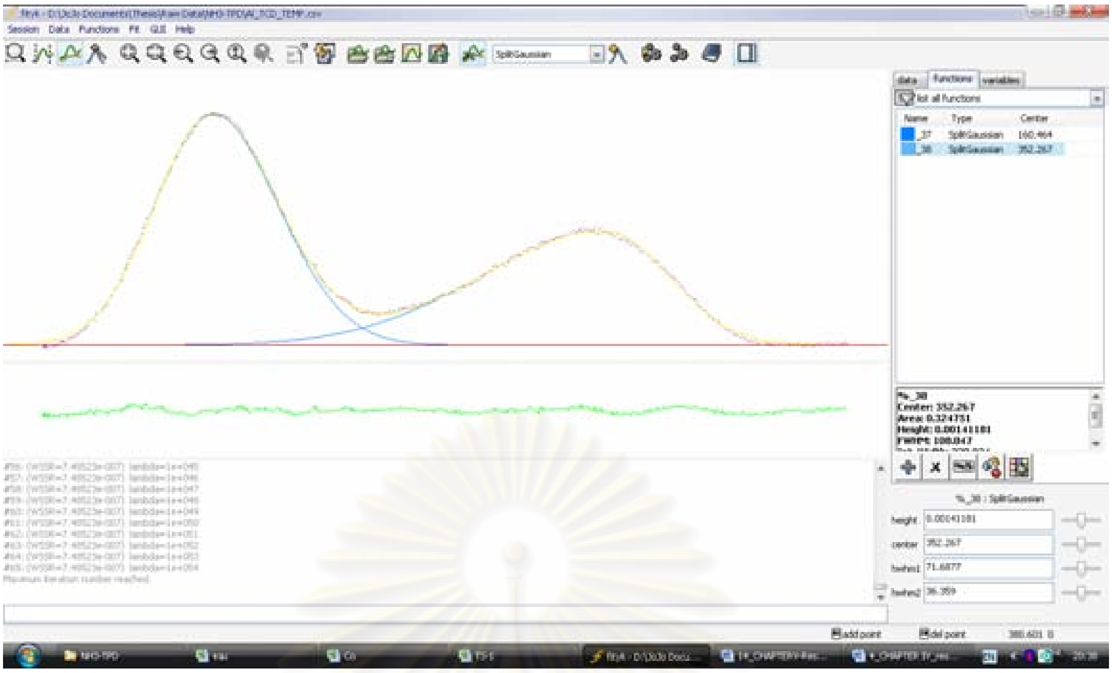


Name	Type	Center
_1	SplitGaussian	153.357
_2	SplitGaussian	313.186

%_1
Center: 153.357
Height: 0.000737214
FWHM: 56.0631

%_1 : SplitGaussian
height 0.000737214
center 153.357
hwhm1 22.4666
hwhm2 33.5964

Figure F6 The data for calculating of acid site ratio of TS-1 from fitting program.

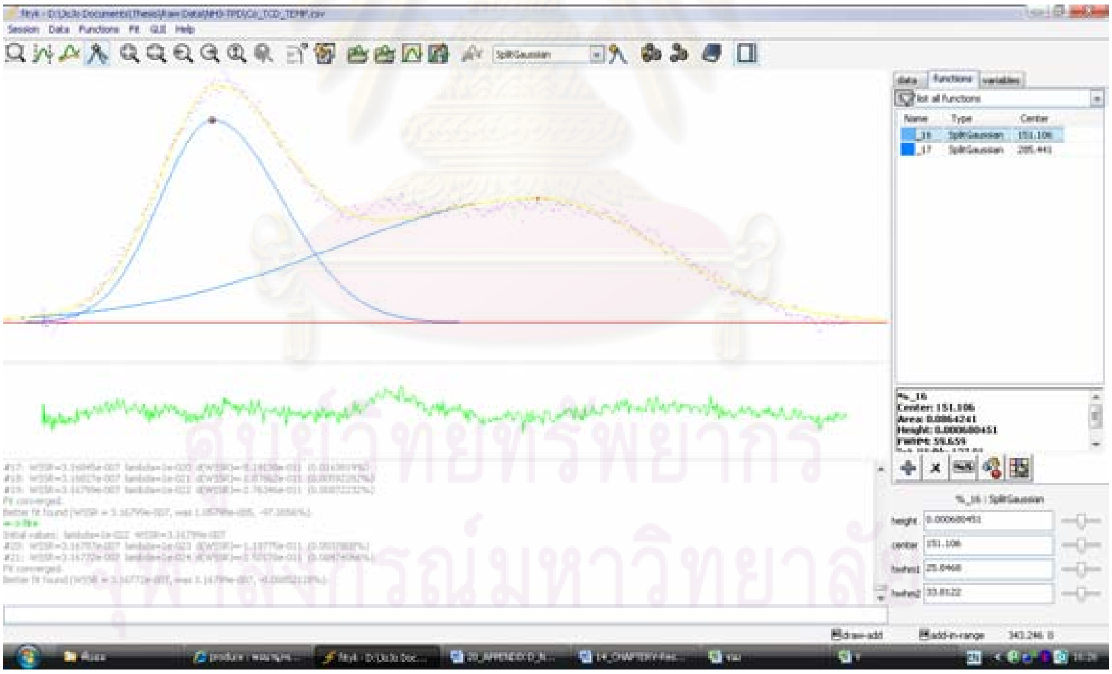


_37 SplitGaussian 160.464
_38 SplitGaussian 352.267

%_38
Center: 352.267
Area: 0.324751
Height: 0.00141181
FWHM: 108.047

%_38 : SplitGaussian
height 0.00141181
center 352.267
hwhm1 71.6877
hwhm2 36.359

Figure F7 The data for calculating of acid site ratio of Al-TS-1 from fitting program.

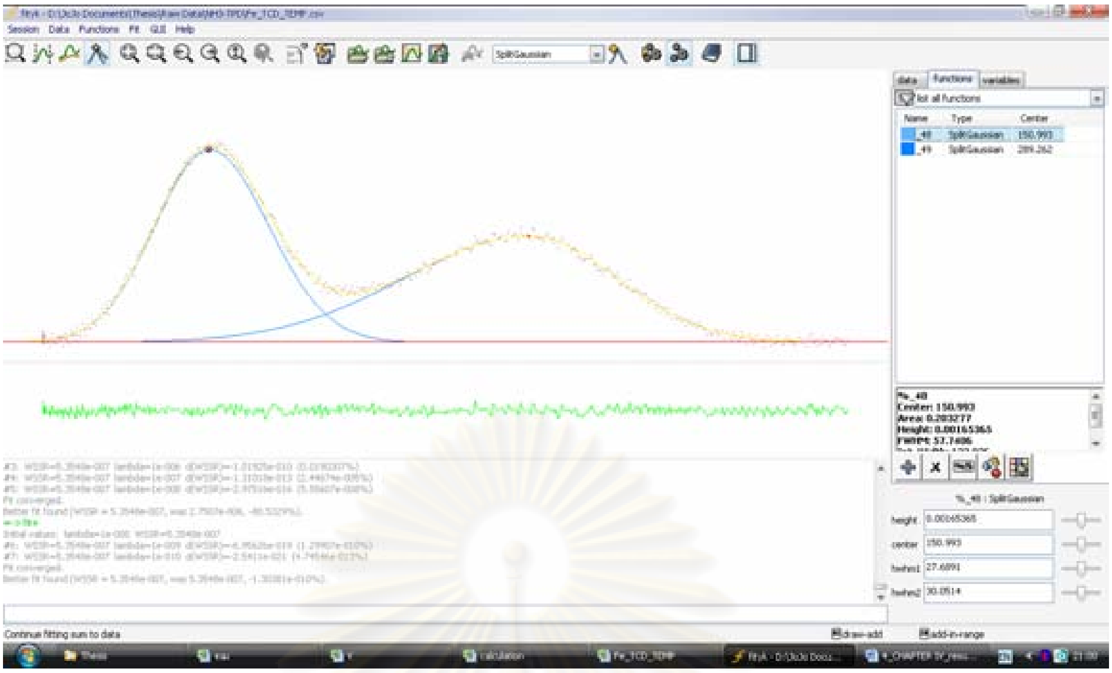


_16 SplitGaussian 151.106
_17 SplitGaussian 285.441

%_16
Center: 151.106
Area: 0.0864241
Height: 0.000680451
FWHM: 58.659

%_16 : SplitGaussian
height 0.000680451
center 151.106
hwhm1 25.0468
hwhm2 33.6122

Figure F8 The data for calculating of acid site ratio of Co-TS-1 from fitting program.

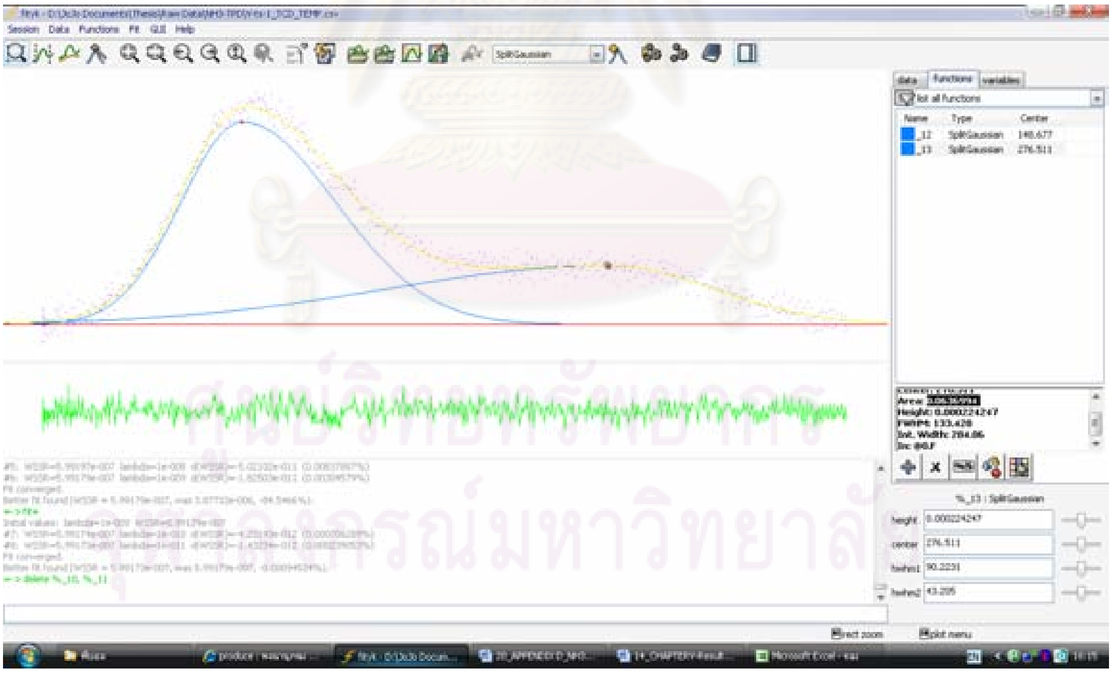


_48 SplitGaussian 150.993
_49 SplitGaussian 289.262

Center: 150.993
Area: 0.283277
Height: 0.00165365
FWHM: 57.7606

height 0.00165365
center 150.993
hwhm1 27.6891
hwhm2 30.0514

Figure F9 The data for calculating of acid site ratio of Fe-TS-1 from fitting program.



_12 SplitGaussian 140.677
_13 SplitGaussian 276.511

Height: 0.000224247
FWHM: 133.428
Int. Width: 284.06

height 0.000224247
center 276.511
hwhm1 90.2231
hwhm2 43.205

Figure F10 The data for calculating of acid site ratio of V-TS-1 from fitting program.

APPENDIX G

CALCULATION OF METAL QUANTITY

Example of the calculation of the metal quantity in VCl_3_A1 catalyst

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

Table G1 Data from XRF technique.

Metal oxide	Concentration
SiO_2	92.66 wt%
CaO	580 ppm
TiO_2	6.47 wt%
Fe_2O_3	1217 ppm
Cu_2O	179 ppm
ZnO	101 ppm
ZrO_2	75 ppm
Al_2O_3	0.64 wt%

Molecular weights of the metal oxides are shown as follow:

Al_2O_3	101.963	Fe_2O_3	159.6922	SiO_2	60.0843
CaO	56.0794	Cu_2O	143.0914	CoO	74.9331
TiO_2	79.9	ZnO	81.3894		
V_2O_5	181.88	ZrO_2	123.2228		

1. Convert concentration in unit ppm to weight%

For example, convert Fe_2O_3 1217 ppm to weight%

$$Fe_2O_3 \text{ 1217 ppm} = \frac{1217}{1{,}000{,}000}\times 100 = 0.1217 \text{ wt\%}$$

2. Mole of metal oxides

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

$$\text{Mole of } Fe_2O_3 = \frac{0.1217}{159.6922} = 7.62\times 10^{-4} \text{ mole}$$

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

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

$$\begin{aligned}\text{Mole of Fe} &= (2)\times(7.62\times 10^{-4}) \\ &= 1.5242\times 10^{-3} \text{ mole}\end{aligned}$$

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

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

$$\text{Mole \% of Fe} = \frac{1.5242\times 10^{-3}}{1.6387} = 0.093 \text{ mole\%}$$

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	Concentration	weight%	mole of metal oxide	mole of cation	Mole% of metal
SiO2	92.66 wt%	92.66	1.542	1.542	94.11
CaO	580 ppm	0.058	1.034x10^{-3}	1.034x10^{-3}	6.311x10^{-2}
TiO2	6.47 wt%	6.47	8.101x10^{-2}	8.101x10^{-2}	4.943
Fe2O3	1217 ppm	0.1217	7.621x10^{-4}	1.524x10^{-3}	9.301x10^{-2}
Cu2O	179 ppm	0.0179	1.251x10^{-4}	2.502x10^{-4}	1.527x10^{-2}
ZnO	101 ppm	0.0101	1.241x10^{-4}	1.241x10^{-4}	7.573x10^{-3}
ZrO2	75 ppm	0.0075	6.087x10^{-5}	6.087x10^{-5}	3.714x10^{-3}
Al2O3	0.64 wt%	0.64	6.277x10^{-3}	1.255x10^{-2}	7.661x10^{-1}
	Total	99.9852	1.632	1.639	100

APPENDIX H

CALCULATION OF ADSORPTION ON CATALYST

The amounts of toluene and ethyl benzene evaluated follow:

$$\text{Mole of sample adsorption} = \frac{\text{mole of blank sample - mole of non-adsorption}}{\text{Surface area of catalyst (m}^2\text{/g)}} \qquad \text{(H1)}$$

Where, the surface area of catalyst are reported in Table 4.3, the mole of blank is mole of sample without catalysts in reactor and the mole of non-adsorption is mole of sample analyzed by gas chromatography, they can be measured as follow:

$$\text{Mole of blank sample} = \frac{\text{Volume of sample feeding} \times \text{Density of sample}}{\text{Molecular weight of sample}} \qquad \text{(H2)}$$

Example, in case of toluene adsorption

$$\text{Mole of non-adsorption} = \text{((area of sample peak from integrator plot on GC-9A)} \times \text{slope of graph sample in Aappendix C)} \qquad \text{(H3)}$$

APPENDIX I

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.

Ethyl benzene

General

Synonyms: phenylethane, EB, ethylbenzol, ethyl benzene

Molecular formula: C_8H_{10}

Physical data

Appearance: colourless liquid

Melting point: -95 °C

Boiling point: 136 °C

Vapour density: 3.7

Vapour pressure: 10 mm Hg at 20 °C

Specific gravity: 0.867

Flash point: 15 °C

Explosion limits: 1 % - 6.7 %

Autoignition temperature: 432 °C

Stability

Stable. Incompatible with oxidizing agents. Flammable.

Toxicology

May be harmful by inhalation, ingestion or through skin contact. Causes severe eye irritation. Skin and respiratory system irritant. Experimental teratogen. Narcotic in high concentration.

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.

Iron(III)chloride hexahydrate

General

Synonyms: ferric chloride, ferric chloride hexahydrate, iron trichloride, iron trichloride hexahydrate, iron(III)chloride hexahydrate
Molecular formula: $FeCl_3$
CAS No: 10025-77-1

Physical data

Appearance: yellow or orange lumps
Melting point: 37 °C
Boiling point: 280 °C
Vapour pressure: 1 mm Hg at 194 °C
Specific gravity: 1.82

Stability

Stable. Incompatible with strong oxidizing agents. Forms explosive mixtures with sodium and potassium. Hygroscopic.

Toxicology

Corrosive - causes burns. Harmful by inhalation, ingestion and through skin contact. Respiratory, eye and skin irritant.
Toxicity data: IPR-MUS LD50 260 mg kg-1

Personal protection

Safety glasses, adequate ventilation.

Aluminium(III)nitrate nonahydrate

General

Synonyms: aluminum nitrate 9-hydrate, aluminium nitrate nonahydrate, aluminum nitrate nonahydrate, nitric acid aluminium salt
Molecular formula: $Al(NO_3)_3 9H_2O$

Physical data

Appearance: white crystalline powder
Melting point: 73 °C
Water solubility: appreciable

Stability

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

Toxicology

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

Personal protection

Safety glasses, adequate ventilation.

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.

Vanadium (III) chloride

General

Synonyms: Vanadium (III) chloride
Molecular formula: VCl_3
Chemical formula : VCl_3

Physical data

Appearance: purple - pink (powder)
Solubility: reacts
Specific Gravity/Density: 3.0000 g/cm3

Stability

Conditions to be avoided: Strong heating.

Substances to be avoided: alkali metals, alkaline earth metals, aluminium in powder form, oxidizing agent, organic nitro compounds, aldehydes, amines, fuming sulfuric acid, phosgene.

Hazardous decomposition products: no information available.

Further information: highly inflammable; hygroscopic, explosive with air in a vapor/gas state.

Toxicology

Harmful if swallowed. Causes burn

Personal protection

Avoid contact with eyes.
Wear suitable protective clothing, gloves and eye/face protection

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 J

LIST OF PUBLICATION

Suchitraporn Sakullimcharoen, Panas Manit and Tharathon Mongkhonsi "Catalytic activity of TS-1 on the hydroxylation of benzene and toluene with hydrogen peroxide in a bubble reactor", Chiang Mai Journal of Science, Chiang Mai university, Thailand, January, 2008, Vol.35 No.1 Page 163-170.

Suchitraporn Sakullimcharoen and Tharathon Mongkhonsi "Hydroxylation of toluene in a bubble reactor using TS-1 and modified TS-1 catalysts", National Grad Research Conference 9th, Burapha university, Thailand, March, 2008, Page 219

VITA

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