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ในปฏิกิริยาไฮดรอกซิเลชันของเบนซีนเป็นฟีนอลโดยใช้ไฮโดรเจนเปอร์ออกไซด์

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
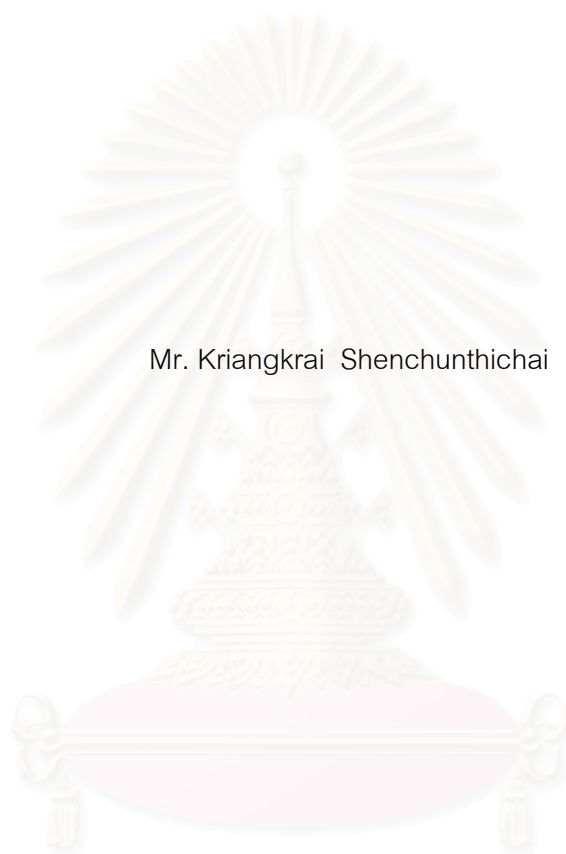สาขาวิชาวิศวกรรมเคมี   ภาควิชาวิศวกรรมเคมี
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CATALYTIC STUDY OF IRON, ALUMINIUM, COBALT AND VANADIUM MODIFIED

TITANIUM SILICALITES-1 IN THE HYDROXYLATION OF BENZENE TO PHENOL

BY HYDROGEN PEROXIDE

Mr. Kriangkrai Shenchunthichai

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

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Thesis Title	CATALYTIC STUDY OF IRON, ALUMINIUM, COBALT AND VANADIUM MODIFIED TITANIUM SILICALITES-1 IN THE HYDROXYLATION OF BENZENE TO PHENOL BY HYDROGEN PEROXIDE
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เกรียงไกร เสนจันทร์ฒิไชย: การศึกษาคุณสมบัติการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาไทเทเนียม ซิลิกาไลต์-1 ที่ถูกปรับปรุงด้วยโลหะเหล็ก, อะลูมิเนียม, โคบอลต์และวาเนเดียมในปฏิกิริยาไฮดรอกซิเลชันของเบนซีนเป็นฟีนอลโดยใช้ไฮโดรเจนเปอร์ออกไซด์ (CATALYTIC STUDY OF IRON, ALUMINIUM, COBALT AND VANADIUM MODIFIED TITANIUM SILICALITES-1 IN THE HYDROXYLATION OF BENZENE TO PHENOL BY HYDROGEN PEROXIDE) อ. ที่ปรึกษา: รศ.ดร.ธราธร มงคลศรี, 84 หน้า.

งานวิจัยนี้เป็นการศึกษาคุณสมบัติการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาไทเทเนียม ซิลิกาไลต์-1 ที่ถูกปรับปรุงด้วยโลหะเหล็ก อะลูมิเนียม โคบอลต์และวาเนเดียม ในปฏิกิริยาไฮดรอกซิเลชันของเบนซีนเป็นฟีนอลโดยใช้ไฮโดรเจนเปอร์ออกไซด์ และอิทธิพลของตัวเร่งปฏิกิริยาที่ถูกปรับสภาพด้วยสารละลายกรดไนตริก ผลการศึกษาแสดงให้เห็นว่าการมีโลหะเหล็ก อะลูมิเนียม โคบอลต์และวาเนเดียมเป็นส่วนประกอบร่วมกับไทเทเนียมในโครงสร้างของซิลิกาไลต์ สามารถเพิ่มอัตราการเกิดปฏิกิริยาสูงกว่าตัวเร่งปฏิกิริยาชนิดซิลิกาไลต์ที่มีโลหะไทเทเนียมประกอบอยู่เพียงชนิดเดียว โดยเฉพาะอย่างยิ่ง ตัวเร่งปฏิกิริยาโคบอลต์ไทเทเนียมซิลิกาไลต์-1 มีอัตราการเกิดปฏิกิริยาสูงที่สุด และหลังจากที่ตัวเร่งปฏิกิริยาถูกปรับสภาพด้วยสารละลายกรดไนตริก พบว่าโครงสร้างตาข่ายของตัวเร่งปฏิกิริยาไม่ถูกทำลาย และไทเทเนียมในโครงสร้างไม่ได้ถูกล้างออก แต่ไทเทเนียมนอกโครงสร้างสามารถถูกล้างออกได้บางส่วน เป็นผลให้ความว่องไวของตัวเร่งปฏิกิริยาสำหรับปฏิกิริยาไฮดรอกซิเลชันของเบนซีนดีขึ้น ความว่องไวของตัวเร่งปฏิกิริยาที่ได้รับการปรับสภาพมีค่าลดลงเรียงตามลำดับ โคบอลต์ไทเทเนียมซิลิกาไลต์-1 วาเนเดียมไทเทเนียมซิลิกาไลต์-1 เหล็กไทเทเนียมซิลิกาไลต์-1 อะลูมิเนียมไทเทเนียมซิลิกาไลต์-1 และไทเทเนียมซิลิกาไลต์-1 โดยตัวเร่งปฏิกิริยาโคบอลต์ไทเทเนียมซิลิกาไลต์-1 เป็นตัวเร่งปฏิกิริยาที่ดีที่สุด เพราะทำให้ไฮโดรเจนเปอร์ออกไซด์ สลายตัวน้อยสุด และมีการดูดซับของฟีนอลบนพื้นผิวต่ำสุดด้วย

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##4870229821: MAJOR CHEMICAL ENGINEERING

KEY WORD: MODIFIED TITANIUM SILICALITE-1/ BENZENE/ PHENOL/ PRETREATMENT

KRIANGKRAI SHENCHUNTHICHAI: CATALYTIC STUDY OF IRON, ALUMINIUM, COBALT AND VANADIUM MODIFIED TITANIUM SILICALITES-1 IN THE HYDROXYLATION OF BENZENE TO PHENOL BY HYDROGEN PEROXIDE. THESIS ADVISOR: ASSOC.PROF. THARATHON MONGKHONSI, Ph.D. 84 pp.

This research has studied the catalytic activity of titanium silicalite-1 (TS-1) catalysts modified by Fe Al Co and V were synthesized, characterized and tested in the hydroxylation of benzene by hydrogen peroxide and the effects of pretreatment with nitric acid aqueous solution on the catalytic activity of catalysts. The results of the reaction show that the Fe Al Co and V incorporated in TS-1 framework promoted the catalytic activity higher than TS-1. Especially, the Co-TS-1 catalyst has the highest catalytic activity. After the catalysts were pretreated by nitric acid aqueous solution, the framework structure of catalyst is not destroyed and titanium in the framework is not removed. But, the extra-framework can be removed partly. As a result, the activity of the pretreated catalysts is improved. The catalytic activity of the investigated catalyst is in the following order Co-TS-1 > V-TS-1 > Fe-TS-1 > Al-TS-1 > TS-1. Co-TS-1 is found to be the best one due to it cause the lowest H_2O_2 decomposition and has the least phenol product deposite on the surface.

Department......Chemical Engineering...   Student's signature.เกียงไกร..เชนจันทร์ธิไชย.

Field of study...Chemical Engineering...   Advisor's signature...........................

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CHAPTER I

INTRODUCTION

Phenol is among the most important intermediates of organic chemistry which plays role as a major raw material. Another use for phenol includes an intermediate stage in the process of producing caprolactam, which is used in nylon and many other man-made fibres. It is also used in the production of drugs, is the starting material in the industrial production of aspirin and synthetic resins to be manufactured, is a polymer of phenol with formaldehyde.

Despite the fact that, the production of phenol via cumene is widely accepted by the industry. The cumene has several significant shortcomings. For instance, Pirutko et al. (2001) reported that it is a multistage synthesis, the intermediate cumene hydroperoxide is explosive, there are ecological problems, and the production rate of the co-product acetone exceeds market demand. Thus, searching for new routes to phenol on direct benzene oxidation. A potential route is the hydroxylation of benzene by hydrogen peroxide. This reaction has gained attention due to several advantages. For example, the hydroxylation reaction is an one-step reaction, the reaction can occur at a relatively low temperature (i.e. 70-80°C), low toxic and/or unwanted by-products are formed. The reaction, however, still has some drawbacks to be overcome. The major drawbacks of the hydroxylation technique are the phase separation between the two reactant and the very low yield of the phenol product.

The hydroxylation of benzene by hydrogen peroxide (H_2O_2) to phenol in the presence of oxidizable metal ions, and super acids is well known. The use of H_2O_2 offers some advantages, such as low cost per oxygen atom and the absence of by-product. These reactions, because of the absence of by-product, are considered as "clean reaction". A heterogeneous catalytic system has advantages over homogeneous systems since it allows simple separation and recovery of the catalyst from the reaction mixture and its subsequent regeneration, once it is deactivated. A direct catalytic method using

heterogeneous, solid catalysts which can efficiently hydroxylate benzene, will have significant advantages and the titanium silicalite-1 (TS-1) catalyst have much more advantage than others. TS-1 has received considerable interest in recent years because of its unique catalytic properties in oxidation involving hydrogen peroxide as the oxidant. TS-1 has the morphology and average pore size nearly same as ZSM-5. Thus the internal mass transfer is slow. Therefore, most of the reaction occurs at the external surface of the catalyst. The limiting step of this reaction should be the external mass transfer or the surface reaction. Consequently, the changing of the feeding system would affect the yield or selectivity of the reaction.

Many researches have been focused on the hydroxylation of benzene with hydrogen peroxide using various type of catalyst. The titanium silicalite-1 (TS-1) is one of the famous catalysts used in this reaction because of its high phenol yield and selectivity. Many researchers studied the effect of operating condition. The most common way, the reaction was study in a stirred slurry reactor without the present of any solvent. Some researches have tried to improve the yield of phenol by adding some solvents, such as acetonitrile, acetone and methanol, to produce a single phase system. For example, Bhaumik et al. (1998) reported that the addition of any solvent that made H_2O_2 and benzene existed in the same phase, the solvent phase, could increase the yield of phenols. This technique, however, possessed a major draw-back, the difficult to separate the phenol product and the unreacted reactants from the solvent phase.

Historically, TS-1 has been widely investigated over various metal loading such as simple metal ions, and metal complexes. From Pirutko et al. (2001) reported that the metal modified TS-1 catalysts gave a higher phenol conversion rate than TS-1. Some of these catalysts have shown potential catalytic activities are summarized in Table 1.1. Therefore, the aim of this research is to investigate the metal modified of TS-1 catalysts by adding Co or V during the synthesis step by a hydrothermal method. It has been reported that loading transition metals to TS-1 up to a level still maintained the MFI structure. In addition, the oxidation properties of metal modified TS-1 and pretreatment

of catalysts in the hydroxylation of benzene with H_2O_2 as the oxidizing agent have never been studied before.

The purpose of this work is to study the oxidation properties of various metal modified TS-1 catalysts including Co-TS-1, V-TS-1, Fe-TS-1 and Al-TS-1 in the hydroxylation of benzene to phenol by H_2O_2 as the oxidizing agent in a stirred slurry reactor where no organic solvents. The research has been scoped as follows:

1) Preparation of M-TS-1 (M = Co, V, Fe or Al) catalysts which have 50 Si to Ti and 150 Si to M ratio by using the incorporation method.

2) Pretreatment of these catalysts with solution 5M HNO_3

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

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

4) Catalytic reactions in a stirred slurry reactor at 70°C to the determine catalytic activity

1.1 The metal modified TS-1

Auther	Year	Catalyst	Method	Process
Thangaraj et al.	1989	Fe-TS-1 Al-TS-1	incoporation	Hydroxylation of benzene with hydrogen peroxide
Petrov et al.	1996	Cu-TS-1	ion-exchange	Carbon monoxide oxidation and nitric oxide reduction reactions.
Pirutko et al.	2001	Al-TS-1 V-TS-1 Cr-TS-1 Fe-TS-1	incoporation	Preparation and catalytic study of metal modified TS-1 in the oxidation of benzene to phenol by NO_2
Jenzer et al.	2001	Pd–Pt/TS-1	incoporation	Epoxidation of propylene with oxygen and hydrogen.
Guo et al.	2004	Ag/TS-1	deposition-precipitation and impregnation methods	Effects of preparation method and precipitator on the propylene epoxidation
Li et al.	2004	Cu-TS-1	ion-exchange and impregnation	Selective catalytic reduction (SCR) of nitrogen oxides (NOx).
Grieken et al.	2004	Al-TS-1	Wetness impregnated	Role of solvent nature in the liquid phase rearrangement of 1,2-epoxyoctane.
Taylor et al.	2005	Au-TS-1	deposition-precipitation	Gas-phase epoxidation of propylene.
Klaewkla et al.	2006	Sn-TS-1	incoporation	Hydroxylation of phenol with hydrogen peroxide

This present work is organized as follows:

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

Chapter II reviews research works on the catalytic activity of metal modified TS-1 catalysts in the hydroxylation of benzene reaction and comments on previous works.

Chapter III presents the theory of this research, studies about the hydroxylation of benzene reaction and its possible mechanism and the properties of TS-1 catalysts.

Chapter IV consists of catalyst preparation, catalyst characterization and catalytic reaction study in hydroxylation of benzene.

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

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

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

CHAPTER II

LITERATURE REVIEW

This chapter divides the reviewed works into two parts, i.e., (a) the catalytic activity of metal modified TS-1 catalysts in the hydroxylation of benzene by H_2O_2, (b) the pretreatment of the catalyst with acid solution to improve the performance of the catalyst. The last section of this review, comments on previous studies that have direct influences on the aims of this study are given.

2.1 Literature review

2.1.1   The catalytic activity of metal modified TS-1 catalysts in the hydroxylation of benzene by H_2O_2

Thangaraj *et al*. (1990) studied the hydroxylation of benzene with H_2O_2 over various zeolites. They found that benzene remained unreacted over silicalite-1, TiO_2 (both amorphous and crystalline), and also in the absence of catalysts. The selectivity for the conversion of H_2O_2 to hydroxyl benzenes decreased in the order TS-1 > Fe-TS-1 > Al-TS-1 > Fe-ZSM-5 > Al-ZSM-5. The selectivity to phenol, however, followed the reverse order. An interesting feature was that while phenol was the only product over pure acid zeolites (Fe-ZSM-5 and Al-ZSM-5), *p*-benzoquinone, the secondary product was formed in appreciable quantities over titanium-containing zeolites (TS-1, Fe-TS-1 and Al-TS-1). The selectivity for *p*-benzoquinone decreased in the order: TS-1 > Fe-TS-1 > Al-TS-1. The acid strength of these zeolites followed the reverse trend i.e., Al-TS-1 > Fe-TS-1 > TS-1. Protonation of phenol over acid zeolites probably suppressed the further electrophilic reaction leading to dihydroxy benzenes.

Bhaumik *et al.* (1998) studied the influence of solvent conditions on benzene catalytic oxidation with H_2O_2. It had been demonstrated that using a tri-phase system (solid-liquid-liquid), in the absence of an organic co-solvent, a considerable increase in the conversion of benzene during the oxidation by the TS-1/H_2O_2 system could be

achieved. Vigorous stirring was needed for the reaction to occur in the tri-phase system. Since the surface of titanium silicalite was relatively hydrophobic in nature, the benzene reactant competed more favorably with water for the diffusion and adsorption under the tri-phase conditions, resulting in higher conversion. Apart from enhancement in activity the present tri-phase method offered distinct advantages in easier product separation and thus contributed to the development of an eco-friendly process.

The use of environmentally detrimental organic solvent created problems in product separation and solvent recycle which were energy intensive steps. Hence, it was important to develop suitable methodology where the oxidation reactions catalyzed by TS-1 using H_2O_2 as an oxidant could be carried out in the absence of organic solvents. In 1999, Kumar *et al.* tried to investigate the enhancement in the reaction rates in the hydroxylation of aromatics over TS-1/H_2O_2 under solvent-free triphase conditions. They reported that the reaction rates of the hydroxylation of aromatics (such as benzene, toluene and anisole) were enhanced under triphase conditions (solid-liquid-liquid) compared to that obtained under biphase conditions in the presence of a co-solvent (solid-liquid). While in the presence of a co-solvent (like acetone, acetonitrile or methanol) a long induction period was observed, in the solvent-free conditions the induction period was almost absent. In the case of substituted benzenes *para*-hydroxy product was predominantly obtained under the triphase conditions. However, in the biphase condition the formation of *ortho*-isomer was preferred. Probable factors responsible for an enhancement in the activity and a change in regions-selectivity were suggested to be: Relative hydrophobic nature and restricted pore dimensions of TS-1; Diffusive resistance faced by the substrate with an organic co-solvent in biphase while such a resistance was minimized in triphase.

Pirutko *et al.* (2001) studied catalytic activity modified some other metals (Al, Ru, Co, V, Cr) in the oxidation of benzene to phenol by N_2O, introduced into the TS-1 matrix at the stage of hydrothermal synthesis. In all cases, the chemical of the initial gel was calculated to provide 1 wt.% of the metal in TS-1, this condition is satisfied for Al and Ru. With Co and Cr, the concentration is higher (1.6 and 1.9 wt.%), and with V it is lower (0.14 wt.%) than the calculated value. The results for Fe-TS-1 containing 0.95 wt.% are 3.84 mole% of phenol in the mixture product. The other

metals 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.

Klaewkla et al. (2006) studied effects of tin incorporation in the TS-1 on the kinetic modelling of phenol hydroxylation to dihydroxybenzenes with aqueous hydrogen peroxide. The kinetic analysis indicates that under the same reaction conditions, titanium-tin silicalite-1(Ti-Sn-S-1) gave a higher phenol conversion rate than TS-1. This was attributed to the Sn active sites. Incorporation of tin influences the initiation of intermediate reactions of products with hydrogen peroxide. Tin increases the rate of benzoquinone conversion to tar; however, it does not affect hydroquinone and catechol reactions.

2.1.2   The pretreatment of TS-1 catalyst

Wang et al. (2004) studied the effect of pretreatment condition of Ag/TS-1 catalysts. The results showed that an increase in the calcination temperature, both the propylene conversion and the selectivity to propylene oxide increased. The catalyst calcined at 450 ºC, exhibited the optimum performance. In case of the effect of calcinations methods of Ag/TS-1 catalysts, they also presented that calcinations methods also had an important effect on the reaction. The optimum activity showed when the catalyst was calcined in air at 450 ºC. The results of the characterization showed that the oxidized Ag species without single electrons played an important role in the epoxidation of propylene.

Liu *et al*. (2004) studied the influence of pretreatment with aqueous solution of CH_3COOK, NaAc, NH_4Ac, NH_4Cl, or HNO_3. They found that the TS-1 framework structure was not destroyed and titanium in the framework was not removed and its surface area changed hardly, but some extra-framework TiO_2 could be removed partly, which led to the slight increase of the crystalline of catalyst and the amount decrease of acid sites on the surface of the catalyst. As a result, the activity, selectivity, utilization of H_2O_2 and the hydroquinone/catechol ratio of product for hydroxylation of phenol were improved. When the TS-1/diatomite catalyst was pretreated by a base solution, the framework silicon of catalyst was dissolved partly

and the framework structure of TS-1 is destroyed, causing the decrease of the crystallinity and surface area of catalyst and the increase of acid sites on the surface of catalyst. As a result, the catalytic activity of the TS-1/diatomite catalyst for hydroxylation of phenol descended or deactivated completely.

2.2 Comment on previous works

From the previous studies e.g. about the reaction, there are many researches about the hydroxylation of aromatic by H_2O_2 over the metal modified TS-1. There are only some researches about the hydroxylation of benzene by H_2O_2 although this is a simple reaction (it yields only two products). From the reviewed literatures, Klaewkla et al. (2006) reported that the metal modified TS-1 catalysts gave a higher phenol conversion rate than TS-1. The effect of pretreatment with acid solution makes them more activity than that unpretreat due to TiO_2 anatase is removed to surface TS-1 catalyst, Liu *et al*. (2004).

Although, the metal modified TS-1 and pretreatment of catalysts can improve the rate of the hydroxylation of benzene reaction, but the previous studies showed no research study the pretreatment of metal modified in the hydroxylation of benzene reaction. Thus, the hydroxylation of benzene by H_2O_2 using the metal modified TS-1 and pretreatment with solution 5M HNO_3 of catalysts under liquid phase operation is chosen to be studied in this research.

CHAPTER III
THEORY

3.1 Hydroxylation of benzene

The hydroxylation of benzene on TS-1 produces phenol as the primary product. Conversion is generally kept low, because introduction of a hydroxyl group activates the aromatic nucleus to further oxidation to hydroquinone, catechol, and eventually to tarry products (Eq. 3.1). In order to overcome the mixing problem of benzene (non polar phase) and H_2O_2 (polar phase), several solvents have been introduced, acetone, methanol, 2-butanone or just water has been reported as suitable reaction media for combing benzene and H_2O_2 phase (Romano *et al.*, 1990; Khouw *et al.*, 1994; Thangaraj *et al.*, 1990). In aqueous solution however, benzoquinone was also found, in appreciable amounts, among the products. An attempt has been carried out by hydroxlysed benzene with a mixture of hydrogen and oxygen, an in situ source of hydrogen peroxide, can be achieved on Pd-containing TS-1 catalyst (Tatsumi *et al.*, 1992). This alternative was in principle, was an easier route to phenol than that based on the preformed oxidant (Clerici and Ingallina, 1998). In practice however, it proved to be less effective, because of faster catalyst decay.
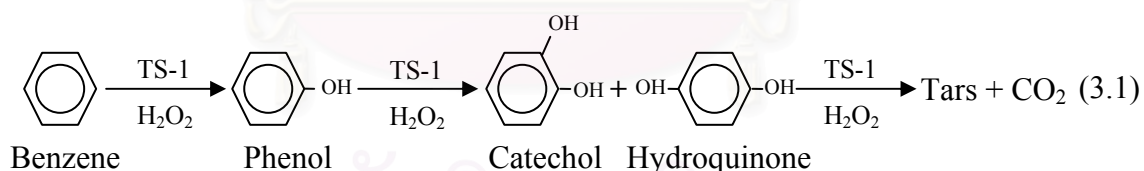
The oxidation of hydrocarbon compounds in aqueous H_2O_2, without added organic solvent (triphase catalysis: solid TS-1 + two immiscible liquids) has been found to be faster than in organic solution (biphase catalysis: solid TS-1 + one liquid). Similarly, the initial rate of epoxidation of propylene was also the highest when conducted in totally aqueous hydrogen peroxide (Clerici and Ingallina, 1998). This specific aspect, i.e. the omission of organic solvent from the reaction mixture, has been the subject of recent detailed investigations on the hydroxylation of aromatic compounds (Kumar *et al.*, 1999; Bhaumik *et al.*, 1998;

Bhaumik *et al.*, 1999). The hydroxylation of benzene under triphase conditions was up to 20 times faster than in acetonitrile or acetone (biphase methodology); this resulted in higher benzene conversion and shorter reaction time. A probable explanation of the reported superiority of triphase catalysis lies in the organophilic properties of TS-1 and in selective adsorption phenomena (Kumar *et al.*, 1999).

The hydrophobic property of the TS-1 surface was believed to play an important role in the hydroxylation reaction. Benzene is expected to compete more favorably with water than with acetonitrile, acetone, or methanol for the adsorption in TS-1 micropores, thus maximizing under tripliase catalysis the probability of interaction with active sites (Weitkamp *et al.*, 1997). This interpretation was supported by competitive adsorption experiments which revealed that the amount of adsorbed benzene in the system TS-1-benzene-H_2O was almost ten times greater than for TS-l-benzeneCH$_3$CN (Bhaumik *et al.*, 1998).

The selectivities under triphase catalysis were also reported to be very high. The high selectivities for benzene-H_2O_2 molar ratios in the range 1-3, benzene conversion and hydrogen peroxide selectivity varying between 74 and 29 % and between 85 and 90 %, respectively, were reported (Bhaumik *et al.*, 1998). The products were phenol (86-95 %), and catechol, hydroquinone, and benzoquinone (14-5 % overall). In acetonitrile solutions, the best selectivity relative to hydrogen peroxide was ca 20 %.

3.2 Molecular sieve and zeolite (Centi.G. et al., 1999)

Zeolite, or crystalline alumino silicates having pore of molecular dimension, occur naturally in the vugs and vesicles of basaltic lava, in volcanic deposits from saline, alkaline lake and nonmarine tuff beds. These naturally occurring zeolites, the first known examples of molecular sieves, were studied scientifically as early as 1760, whereas their selective adsorption and ion-exchanged properties have been known for decades. Today, zeolites and other molecular sieves, the crown jewels of catalysis, promise to revolutionize chemicals manufacture, petroleum refining and coal and/or natural gas conversion processes through the concept of catalysis by molecular design.

3.2.1 Composition of molecular sieves

Strictly speaking, the term molecular sieve refers to a class of crystalline materials having a range of compositions that exhibit shape-selective adsorption and reaction properties, whereas the term zeolite refers to the shape-selective materials composed only of alumino silicates. The range of materials that make up molecular sieves includes carbon, silica, aluminosilicates, aluminophosphates, metallosilicates (e.g. gallosilicates, chromo silicates, borosilicates, and ferrisilicates) and metalloaluminates (e.g. germinium aluminates). In fact, the list of cations that can be incorporated into molecular sieve frameworks has been expanded to include 16 or more elements (Si, Al, Ga, Ge, Be, Li, Mg, Ti, Cr, Mn, Fe, Co, Zn, B, C, P etc.).

3.2.2 Composition and structure of zeolites

Zeolites or aluminosilicates have the general formula $M_v(AlO_2)_x(SiO_2)_y.zH_2O$; the AlO_2 and SiO_2 species are the fundamental units that share oxygen ions to form tetrahedral AlO_4 and SiO_4 building blocks for the zeolite unit cell. Thus, the framework of a zeolite is made up of aluminum and silicon tetrahedral, while metal or hydrogen cations (M) occupy exchangeable cationic sites. Table 3.1 shows the unit cell composition for several important Na-exchanged zeolites along with aperture size (limiting pore size). Note that because the silicon ion has a charge of +4 and aluminium +3, the number of Na^+ ions required for charge equalization is equal to the number of aluminum ions.

The synthesis of zeolites from its basic building blocks is illustrated in Figure 3.1. A typical aluminosilicate is formed by polymerization of SiO_4 and AlO_4 tetrahedra to form sheet-like polyhedra (squares and hexagons) which in turn form cubes, hexagonal prisms and truncated octahedral (14-sided). These three-dimensional tertiary building blocks in turn are arranged regularly to form a superstructure inside which exist pores and a supercage. Each supercage has a characteristic window size aperture which blocks entry of sufficiently large molecules, i.e. the sieve effect.

Table 3.1 Composition and limiting pore diameters for common zeolites (Farrauto and Bartholomew, 1997)

Type	Composition per unit cell				Aperature Size (Å)
	Na	AlO_2	SiO_2	H_2O	
A	12	12	12	27	4.2
Faujasite X	86	86	106	264	8.0
Faujasite Y	56	56	136	264	8.0
Erionite	4.5	9	27	27	4.4
Mordenite	8	8	40	24	6.6
Pentasil (ZSM-5)	9	9	87	16	5.5
Pentasil (Silicate)	0	0	96	16	5.5

3.2.3 Pore structure of molecular sieves

The zeolites listed in Table 3.1 are just a few of the many possible molecular sieve structures. According to Vaughan, 1988: 'few fields of chemistry offer such chemical diversity; although only about 60 structures are known, tens of thousands of theoretical structures are possible.'

Probably the simplest level of classifying molecular sieve structure is in terms of pore diameter and ring size. By convention, ring size is specified by the number of T atoms or TO_4 units where T = Si, Al, P or B. Pore diameters of aluminosilicate molecular sieves (A, erionite, pensil, mordenite and faujasite) range from 3 to 8 Å, whereas ring sizes range from 8 Å for erionite to 12 Å for Y-Zeolite.

3.2.4 Acidity

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

Bronsted and Lewis acidities of zeolites play important roles in their abilities to catalyze various hydrocarbon reactions, e.g. cracking and isomerization.
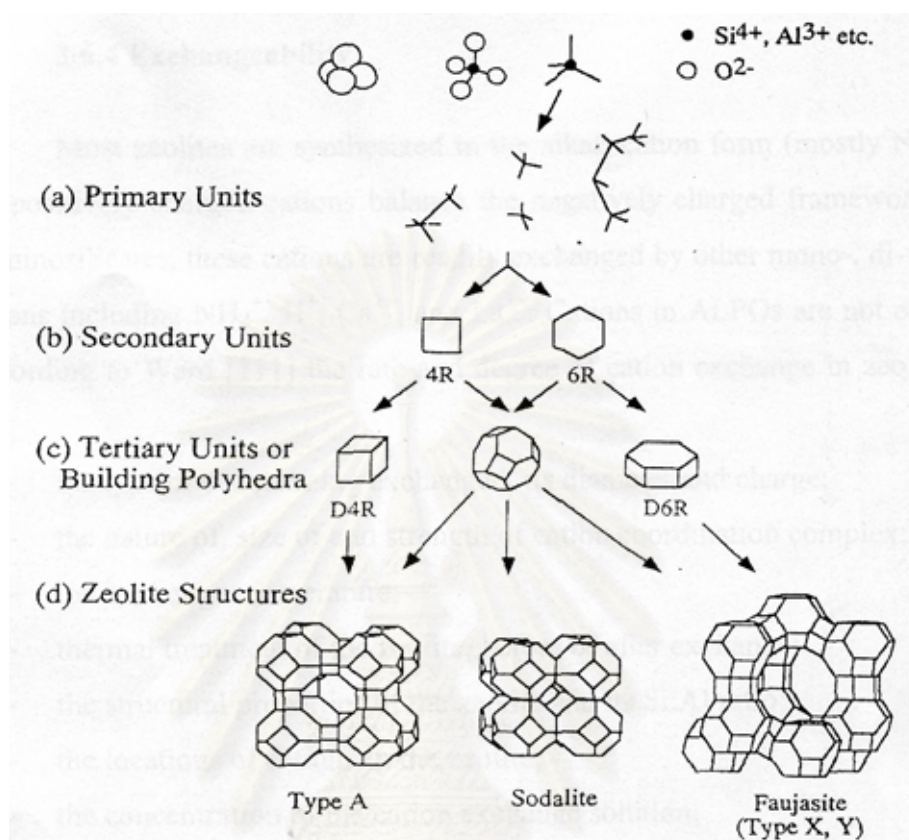
Figure 3.1 Formation of three common zeolites from primary SiO_4 and AlO_4 tetrahedral units through a combination of secondary ring units, and ultimately different mixes tertiary polyhedra; note,however, that all three use the same structural polyhedron (cuco-octahedron) in the final construction (Farrauto and Bartholomew, 1997)

3.2.5 Thermal stability

The thermal stability of zeolites increases with increasing silica content and by exchange with rare earth cations. Most sieves are uncharged by dehydrating to 400 °C; high silica (ultrastabilized forms prepared by steam pre-treatment) and rare earth-exchanged sieves are stable to 700-800 $^{\circ}$C. Generally, extensive dehydration causes loss of Bronsted acidity due to the removal of OH or silanol surface groups.

Thermal treatment of zeolites in the presence of water normally leads to dealumination. In fact, it is one of the recommended methods for preparing ultrastable zeolites. Moderate dealumination generally increases catalytic activity or leaves it unchanged, whereas advanced dealumination leads to a decrease in activity due to a loss of active sites and ultimately collapse of the zeolite structure. For example, dealumination of mordenite significantly changes important chemical and physical properties such as crystal structure, thermal stability, sorption capacity and acidity, as well as catalytic properties. Maximum thermal stability is reached for an $SiO_2:Al_2O_3$ ratio of about 19. The sorption capacity towards water is highly reduced after dealumination because of the absence of strong polarizing cations which can dissociate water to strongly adsorbed hydroxy groups; accordingly, the number of Brönsted acid sites also decreases. Nevertheless, the hydrocarbon cracking activity of mordenite increases with increasing Si:Al ratio.

3.2.6 Shape selectivity

Many reactions involving carbonium intermediates are catalyzed by acidic zeolite. With respects to a chemical standpoint the reaction mechanisms are not fundamentally different with zeolites or with any the acidic oxides. What zeolite add is shape selectivity effect. 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. These types of selectivity are illustrated in Figure 3.2.

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.

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.

Reactant Selectivity

Product Selectivity

Transition State Selectivity
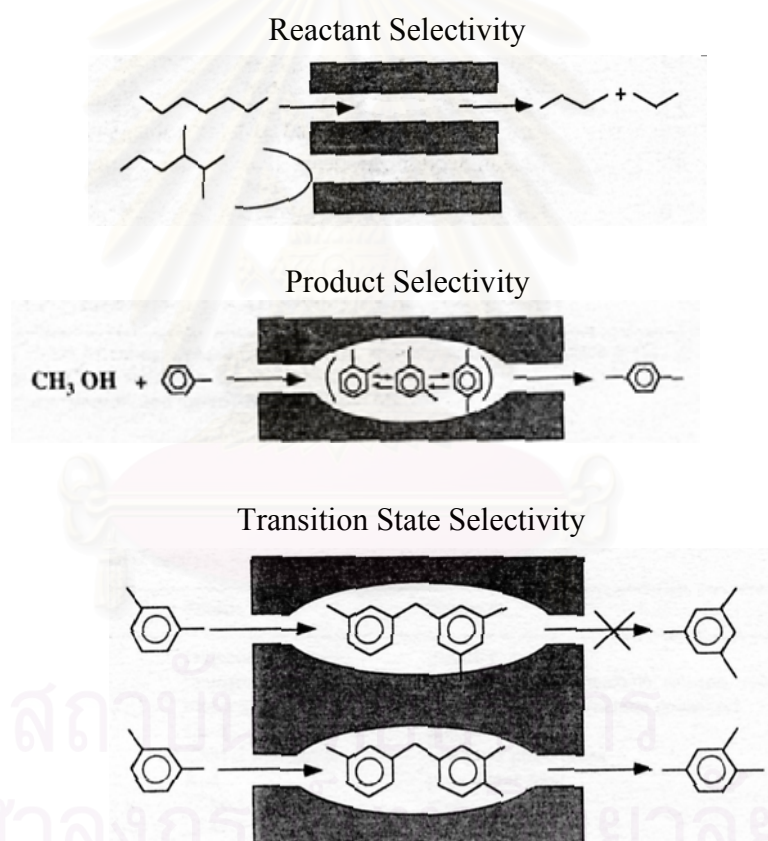
Figure 3.2 Diagram depicting the three type of selectivity (Farrauto and Bartholomew, 1997)

3.3 Titanium silicalite (Notari, 1989)

Titanium silicalite is an interesting material obtained by isomorphic substitution of trivalent metals or tetravalent metals in the framework of crystalline aluminosilicates or silicates. Titanium silicalites with MFI (TS-1) and MFI/MEL (TS-2) structures have been used in several oxidation reactions with H_2O_2 as the oxidizing agent (Centi et al., 2001).

Titaniun 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^{IV} compounds immediately shows that Ti^{IV} 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^{IV} 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^{IV}, 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^{IV} with Ti^{IV} it seems justified to represent TS-l as a silicalite in which few Ti^{IV} have taken the place of Si^{IV}. The interpretation of the catalytic activity of TS-l must take into consideration the role played by these few Ti^{IV}: 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^{IV} in the crystal lattice is at random; since the Si/Ti ratio is in the range 40 - 90 in typical preparations, most Ti^{IV} must be isolated from each other by long sequences of -O-Si-O-Si-O-. If Ti^{IV} replaces a Si^{IV} 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 streching 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^{IV} are occupied by Si^{IV} 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

$$
\begin{array}{ccc}
\text{O} & \text{OH} & \text{O} \quad\quad \text{HO} \quad\quad \text{O}\\
\diagdown\text{Si}\diagup & & \parallel \quad\quad\quad\quad \diagdown\text{Si}\diagup\\
\diagup \quad\quad \diagdown & & \text{Ti} \quad\quad\quad\quad \diagup \quad\quad \diagdown\\
\text{O} \quad\quad \text{O} & & \quad\quad \text{O} \quad\quad\quad\quad\quad \text{O}
\end{array}
\qquad (3.2)
$$
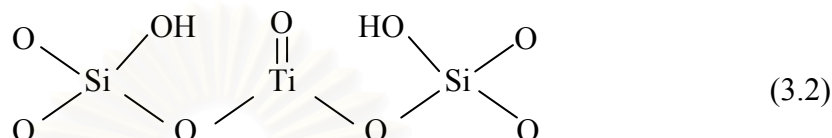
Other more elaborated and detailed representations could be given, should the present model prove inadequate to interpret all experimental facts. Ti^{IV} in TS-1 maintains the strong affinity of soluble Ti^{IV} salts for H_2O_2 and in fact the addition of H_2O_2 gives rise to a strong yellow colour which can be attributed to the formation of surface titaniunperoxocompounds which can be in the hydrated or dehydrated form and which constitutes the actual oxidants.
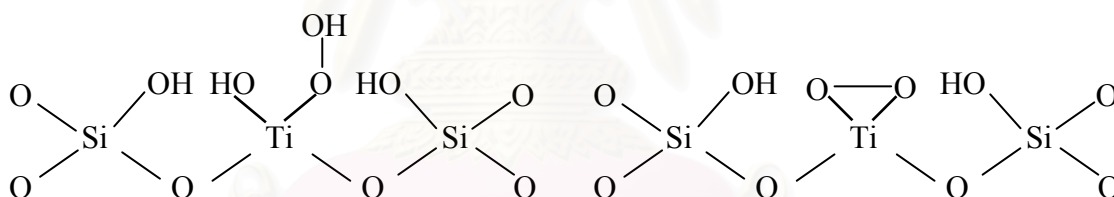
Work carried out on Mo(VI) and W(VI) peroxocompounds (Amato *et al.*, 1986) has demonstrated that peroxocompounds can act as oxidants in stoichiometric epoxidations involving a nucleophilic attack of the substrate to the peroxidic oxygen: in the presence of excess H_2O_2 the peroxo compound is regenerated and this accounts for the catalytic nature of the reaction. It seems reasonable to assume that a similar mechanism operates in the case of Ti(IV) peroxocompounds. The relevance of isolated Ti^{IV} and the connection with catalytic performances appears to hold also for the TiO_2/SiO_2 catalyst. In fact high epoxide selectivities are obtained when TiO_2 is distributed on high surface area SiO_2 and its concentration is limited to 2% (Sheldon, 1980). It is very likely that at this low concentration Ti^{IV} are isolated and surrounded by Si^{IV}. Furthermore, SiO_2 or TiO_2 alone, or physical mixtures of SiO_2 and TiO_2 or various metal titanates exhibit no significant activity. Similarly, supporting TiO_2 on

carriers different from SiO_2 like Al_2O_3, MgO or ZrO_2 leads to catalysts whose activity is lower or nil. One piece of evidence seems very convincing: when the TiO_2 concentration on the catalyst is reduced from 4% to 0.4%, all other conditions being equal, an increase in epoxide selectivity is obtained. The only effect that a reduction in the concentration of TiO_2 can have is an increase in the degree of dispersion of each Ti^{IV}: chances for each Ti^{IV} of having Si^{IV} as near neighbours increase, as does the selectivity of the catalyst. The correlation between the isolated Ti^{IV} and selectivity of the catalyst in epoxidation could be due to the fact that on Ti^{IV} having other Ti^{IV} as near neighbours, a mechanism proceeding through a bimolecular interaction of surface peroxo species could be operating which would give rise to a high decomposition rate of H_2O_2 or hydroperoxides to O_2. This mechanism could not operate on perfectly isolated Ti^{IV}.

$+ O_2 + 2H_2O$
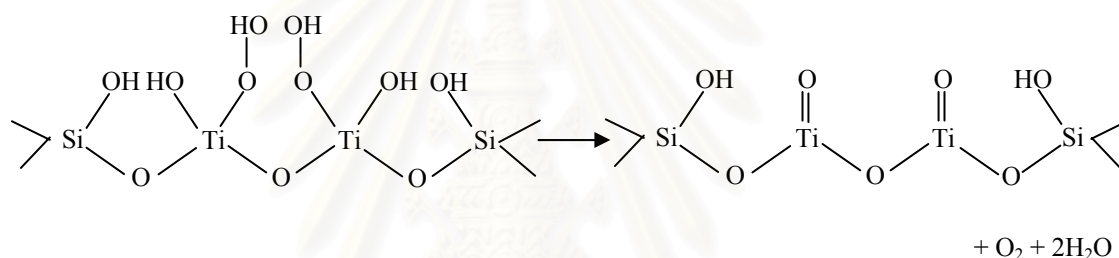
Low decomposition of H_2O_2 (or hydroperoxides as well) means greater stability of titanium peroxo compound whose reduction can only be carried out by the organic substrate with increased yields of useful oxidized products. When the different results between TS-1 and TiO_2/SiO_2 in the hydroxylation of phenol are analyzed the existence of a "restricted transition state selectivity" must be assumed to explain the small amount of tars formed.

CHAPTER IV

EXPERIMENTAL

The experimental in this chapter is divided into three major parts: (1) catalyst preparation, (2) catalyst characterization, and (3) reaction study. The chemicals, apparatus and procedures for catalyst preparation are explained in section 4.1. The composition, structure, surface properties, acidity of the catalyst characterised by various techniques such as XRF, BET, XRD, FT-IR and NH_3-TPD are discussed in section 4.2. Finally, the details of the reaction study are illustrated in section 4.3.

4.1 Catalyst preparation

4.1.1 Chemicals

All chemicals used in this preparation procedure of M-TS-1 catalysts are following in Table 4.1.

Table 4.1 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(II)chloride	Analytical	Fluka
Iron(III)chloride hexahydrate	Analytical	Merck
Aluminium(III)nitrate nonahydrate	Analytical	APS

4.1.2 Preparation Procedures

The preparation procedure of M-TS-1 by rapid crystallization method is shown in Figure 4.1, while the reagents used are shown in Table 4.2.

Table 4.2 Reagents used for the preparation of M-TS-1 : Si/Ti = 50, Si/M = 150 (Appendix A)

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

| A1 SOLUTION | B1 SOLUTION | C1 SOLUTION |
| A2 SOLUTION | B2 SOLUTION | C2 SOLUTION |

HOMOGENIZED MIXING
OF
GEL-PRECIPITATION

HOMOGENIZED MIXING
OF
DECANT-SOLUTION

GEL-SOLUTION

DECANT-GEL

GEL PRECIPITATE

DECANT-SOLUTION

MILLING

HYDROTHERMAL TREATMENT
IN AUTOCLAVE

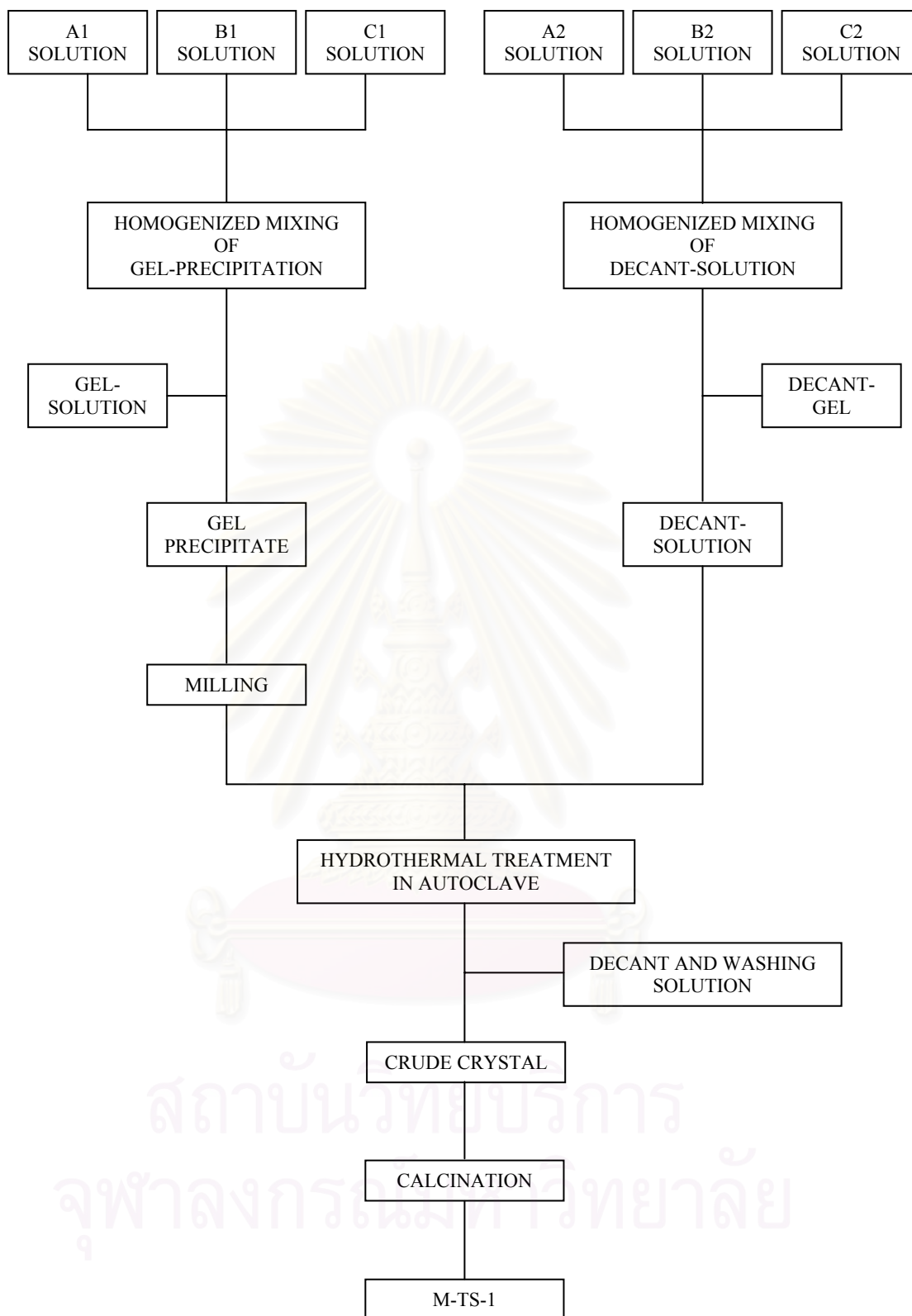DECANT AND WASHING
SOLUTION

CRUDE CRYSTAL

CALCINATION

M-TS-1

Figure 4.1 The preparation procedure of M-TS-1 by rapid crystallization method

4.1.2.1 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 dropwise with vigorous stirring using a magnetic stirrer at room temperature. The pH of the gel mixture was maintained within the range 9-11 because this pH range is suitable for precipitation. H_2SO_4 (conc.) or NaOH solution were used to adjust pH of the gel mixture to an appropriate level if it was necessary. 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 $\rightarrow$ centrifuge (to remove liquid out) 15 min $\rightarrow$ milled 15 min $\rightarrow$ centrifuge 15 min $\rightarrow$ milled 30 min $\rightarrow$ 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.

4.1.2.2 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 $^{\circ}$C with a heating rate of 2 $^{\circ}$C/min, and then heating up to 210 $^{\circ}$C

with a heating rate of 12 $^{\circ}$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 $^{\circ}$C for at least 24 h.

4.1.2.3 Calcination

The dry crystals were calcined in an air stream at 550 $^{\circ}$C and held at that temperature for 7 h, by heating them from room temperature to 550 $^{\circ}$C at a heating rate of 8.6 $^{\circ}$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.

4.1.3 Pretreatment catalysts

3 g of M-TS-1 and TS-1 were placed into a round bottom flask and then 14 ml of 5M HNO_3 aqueous solution was added. After reflux at 80°C for 3 h, the pretreated catalyst was filtered, washed with distilled water until pH 7, dried at 110°C and calcined at 540°C for 7 h in static air.

4.2 Catalyst characterization

4.2.1 X-Ray Fluorescence Spectrometer (XRF)

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

4.2.2 BET surface area measurement

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

4.2.3 X-Ray Diffraction (XRD)

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

4.2.4 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

4.2.5 NH$_3$ Temperature Programmed Desorption (NH$_3$-TPD)

Temperature programmed desorption of ammonia (NH$_3$-TPD) was used to determine the acid properties of catalysts. NH$_3$-TPD were carried out using a flow apparatus. The catalyst sample (0.1 g) was treated at 550°C in helium flow for 1h and then saturated with 15 %NH$_3$/He mixture after cooling to 100 ^{o}C. After purging with helium at 100 ^{o}C for 1 h to remove weakly physisorbed NH$_3$, the sample was heated to 550 ^{o}C at therate of 10 ^{o}C/min in a helium flow of 50 cm^3/min. The amount of acid sites on the catalyst surface was calculated from the desorption amount of NH$_3$. It was determined by measuring the areas of the desorption profiles obtained from the Micromeritics Chemisorb 2750 analyzer

The deconvlution of NH$_3$-TPD peak was carried out with the "fityk" curve fitting programme. The peaks were assumed to be Gaussian with showness shape (using parameter 'SplitGaussian' in the programme).

4.3 Reaction study in hydroxylation of benzene

The hydroxylation of benzene with H$_2$O$_2$ (30 wt% in water, Merk) was carried out in a 250 ml, water jacketed, there-necked, glass flask fitted with a condenser and a mechanical stirrer placed in a stirring block heater as shown in Figure 4.2. The reaction was performed at atmospheric pressure. Typically, 1 g of a catalyst was reacted with 0.88 g of benzene (99.8 wt%, PS) and 1.27 g of aqueous H$_2$O$_2$ (benzene to H$_2$O$_2$ molar ratio equals to 1 to 1) where no organic solvents. The additional water 70 g, apart from coming through aqueous H$_2$O$_2$, was used for dispersion of the catalyst in this heterogeneous system and to maintain the dilution level. Generally, H$_2$O$_2$ was slowly injected drop-wise using a 1 ml syringe.

The detailed studies on the influence of various reaction parameters that affect the performance of M-TS-1 and TS-1 in hydroxylation of benzene as followings:

- The effect of various catalyst including TS-1, Co-TS-1, V-TS-1, Fe-TS-1 and Al-TS-1.
- The effect of pretreatment catalysts with aqueous solution of 5M HNO$_3$.
- The temperature effects were studied by carried out the reaction at different temperatures: 50, 60, 70, and 80 $^{\circ}$C.
- The concentration effects, the reactions were carried out with different molar ratios of benzene to H$_2$O$_2$ as follows: 2 to 1, 3 to 2, 1 to 1, and 1 to 2.
- The effect of reaction time was various between 0.25 to 4 hr.

The products were collected at various intervals of reaction times and analyzed by a gas chromatograph equipped with a FID detector (SHIMADZU GC9A). The operating conditions of the GC are listed in Table 4.3. The chromatogram data were converted into mole of phenol using a calibration curves (Appendix C).

Table 4.3 Operating conditions for gas chromatograph

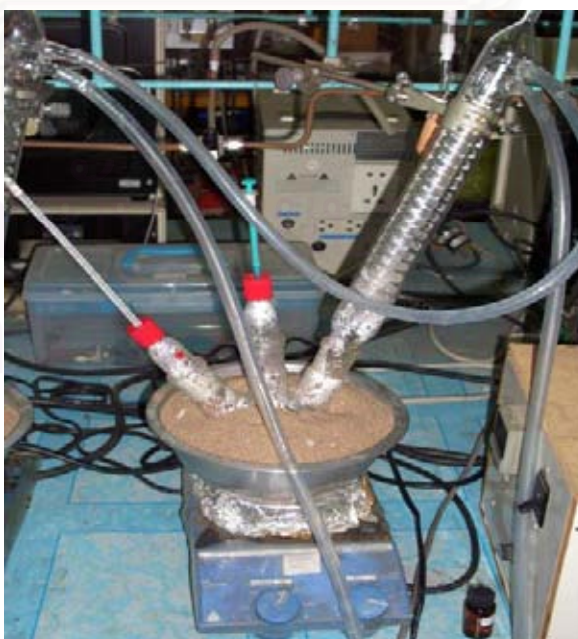| Gas chromatograph	SHIMADZU GC9A
Detector	FID
Packed column	GP 10% SP-2100
Carrier gas	N_2 (99.999%)
Carrier gas flow rate (ml/min)	30
Injector temperature (^{o}C)	250
Detector temperature (^{o}C)	250
Initial column temperature (^{o}C)	110
Programme rate (^{o}C/min)	10
Final column temperature (^{o}C)	170
Analyzed chemicals	Benzene and Phenol

Figure 4.2 The benzene hydroxylation reactor

CHAPTER V

RESULTS AND DISCUSSION

In Chapter V, results and discussion are divided into two sections. The first section is the result of characterization of catalysts using XRF, BET, XRD, FT-IR, and NH_3-TPD. The second section is the results of catalytic hydroxylation reaction of benzene to phenol.

5.1 Catalyst 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.

5.1.1 Determination of composition by 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 5.1, the measured concentrations of the metals in the pretreated and unpretreated M-TS-1 are given. As can be seen, in the unpretreated samples, the Co, V, Fe, and Al concentrations added in the synthesized procedure were 0.0971, 0.0964, 0.1001, and 0.1025, respectively. In addition, the pretreated of samples, the decrease of the Co, V, Fe, and Al concentrations from 0.0971 to 0.0271, 0.0964 to 0.0215, 0.1001 to 0.0558, and 0.1025 to 0.0658, respectively. Furthermore, the pretreatment of samples were found that TiO_2 in framework was decreased.

Table 5.1 XRF analysis of M-TS-1 and TS-1

Sample	No pretreatment						With pretreatment					
	%Si	%Ti	%M	%Si/Ti	%Si/M	%TiO$_2$	%Si	%Ti	%M	%Si/Ti	%Si/M	%TiO$_2$
TS-1	32.15	0.44	none	72.80	none	1.75	32.97	0.22	none	150.63	none	0.77
Co-TS-1	31.90	0.52	0.0971	61.50	328.51	2.05	33.06	0.12	0.0271	276.86	1220.61	0.47
V-TS-1	32.03	0.45	0.0964	71.76	332.40	1.77	33.05	0.11	0.0215	282.24	1535.20	0.43
Fe-TS-1	32.66	0.49	0.1001	66.03	324.03	1.96	32.92	0.21	0.0558	158.67	590.22	0.78
Al-TS-1	32.78	0.45	0.1025	72.77	319.86	1.79	33.09	0.18	0.0658	182.59	502.72	0.77

It should be noted here that the corporation of each cation (Si, Ti, Co, V, Fe, and Al) into the MFI structure is in random form. Therefore, it is impossible to fixed the ratio of Si/Ti of the synthesized catalyst for each sample. In addition, since the amount of titanium is very low compared with the amount of Si, the ratio Si/Ti can change rapidly when the amount of titanium only a little bit changes.

5.1.2 Determine of surface area by BET

The surface areas of M-TS-1 and TS-1 samples are presented in Table 5.2. All samples have BET surface areas and average pore size diameter in same the order. A small increase in the BET surface area and a small decrease in the average pore size diameter of each sample were observed after the treatment. This is likely due to the removal of some species that block the small pores.

Table 5.2 The composition and surface area of M-TS-1 and TS-1 samples.

Sample	No pretreatment			With pretreatment		
	A_{BET} (m^2/g)	Pore volume (cm^2/g)	Pore size(A°)	A_{BET} (m^2/g)	Pore volume (cm^2/g)	Pore size(A°)
TS-1	323.34	0.1952	31.1510	328.73	0.2468	30.0343
Co-TS-1	350.62	0.2379	29.5347	361.62	0.2440	26.9853
V-TS-1	329.58	0.1970	28.1347	354.87	0.2450	26.7337
Fe-TS-1	334.54	0.2063	27.0979	344.27	0.2205	25.6203
Al-TS-1	328.83	0.2203	27.6349	331.71	0.2235	26.9555

5.1.3 X-ray diffraction (XRD)

Figures 5.1 and 5.2 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)]. They have no peak at 2theta ≈ 25.3°, represents the anatase TiO_2 phase. Therefore, all TS-1 synthesized using TPABr as template does not contain anatase. After the catalysts were pretreated, it is found that the structures are not destroyed by the pretreatment with HNO_3.
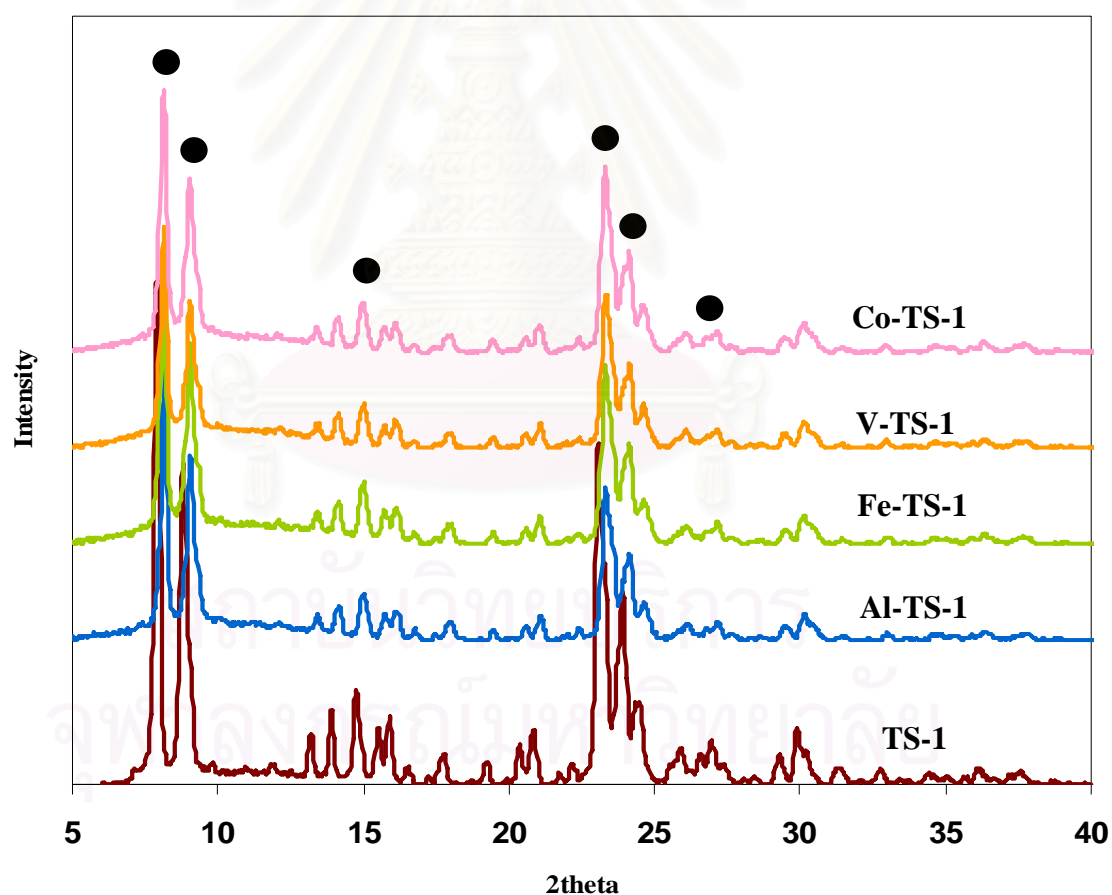

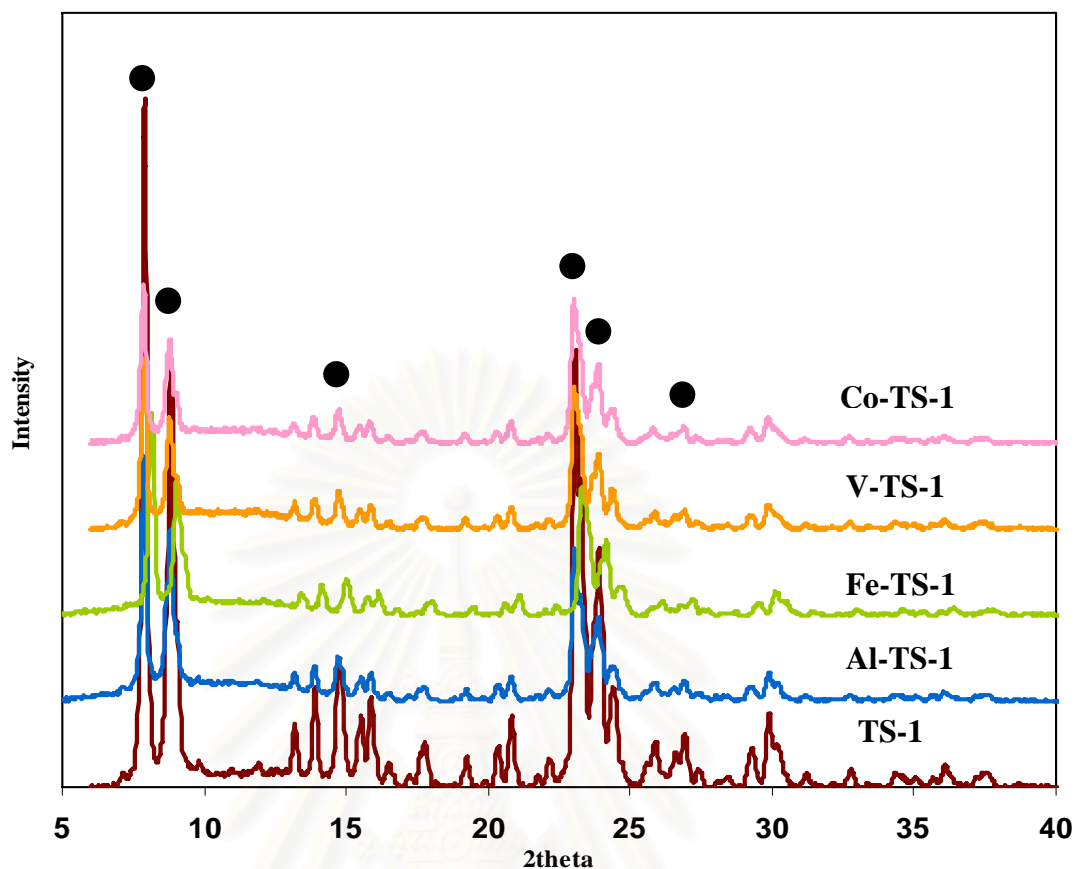**Figure 5.1** The XRD patterns of M-TS-1 and TS-1 before treatment.

Figure 5.2 The XRD patterns of M-TS-1 and TS-1 after treatment.

5.1.4 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 (Figures 5.3, and 5.4) 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}. After pretreatment with 5M HNO_3 (Figure 5.4), it is found that the peak at about 960 cm^{-1} does not weaken, which means that the framework titanium species had not been washed off by HNO_3
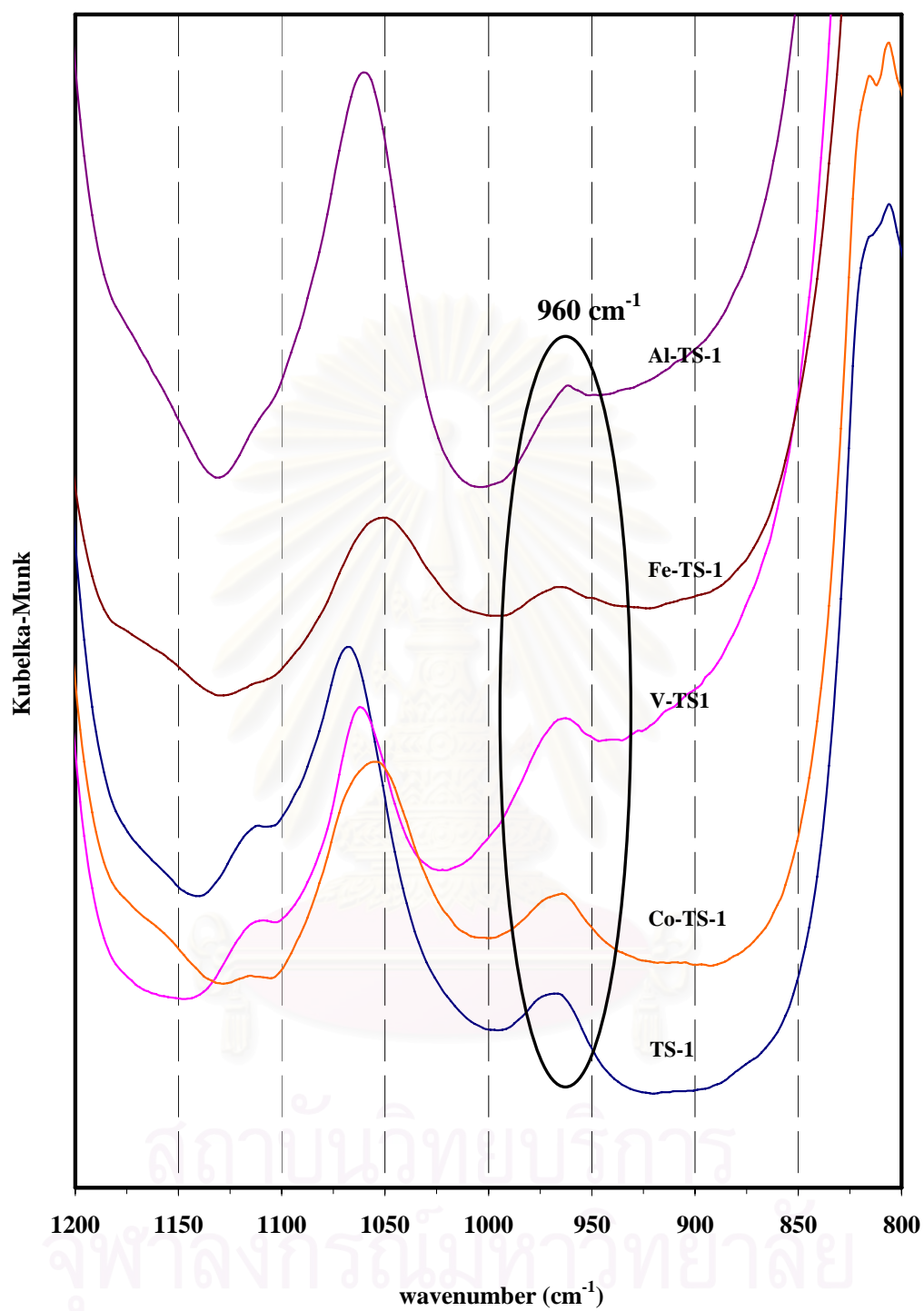
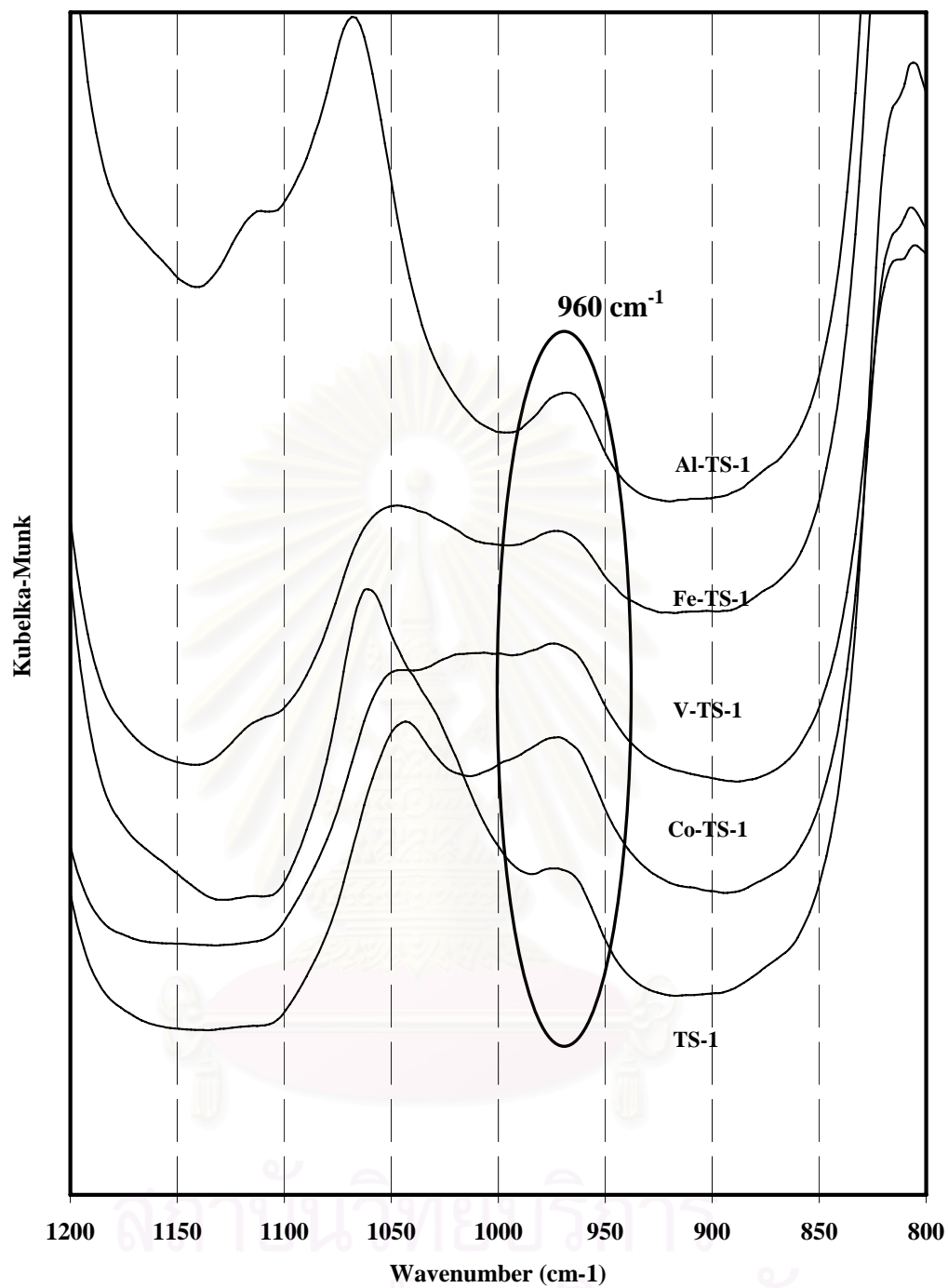**Figure 5.3** IR spectra of M-TS-1 and TS-1 before treatment.

Figure 5.4 IR spectra of M-TS-1 and TS-1 after treatment.

5.1.5 Temperature Programmed Desorption (TPD)

NH_3-TPD was used to determine the strength and amount of the acid site of the catalysts. The results are shown in Figures 5.5-5.23 and Table 5.3. Deconvolution details of the catalyst sample without any pretreatment are shown in Figures 5.5-5.18 while Figures 5.19-5.23 illustrate the deconvolution details of the catalysts after the pretreatment. The deconvolution is performed by using a freeware programme named "fityk". The peak fitting process 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 B.

It is found that each NH_3-TPD profile can be deconvoluted into two main peaks. The first peak, will be named here "the weak acid site", appears around 120-145°C. The second peak, will be named here "the strong acid site", appears around 202-403°C.

The results of samples showed in Table 5.3 indicates that the quantities of the acid site. The M-TS-1 catalysts without pretreatment, the acid strength (which can be determined from the location of the peak) on the surface of the catalysts more than the TS-1 catalyst. After the M-TS-1 catalysts were pretreated with the aqueous solution of 5M HNO_3, the acid strength is higher than the TS-1 catalyst. The Co-TS-1 without pretreatment and pretreatment give the highest acid, 111.6636 μmol/g, and 169.6688 μmol/g, respectively.
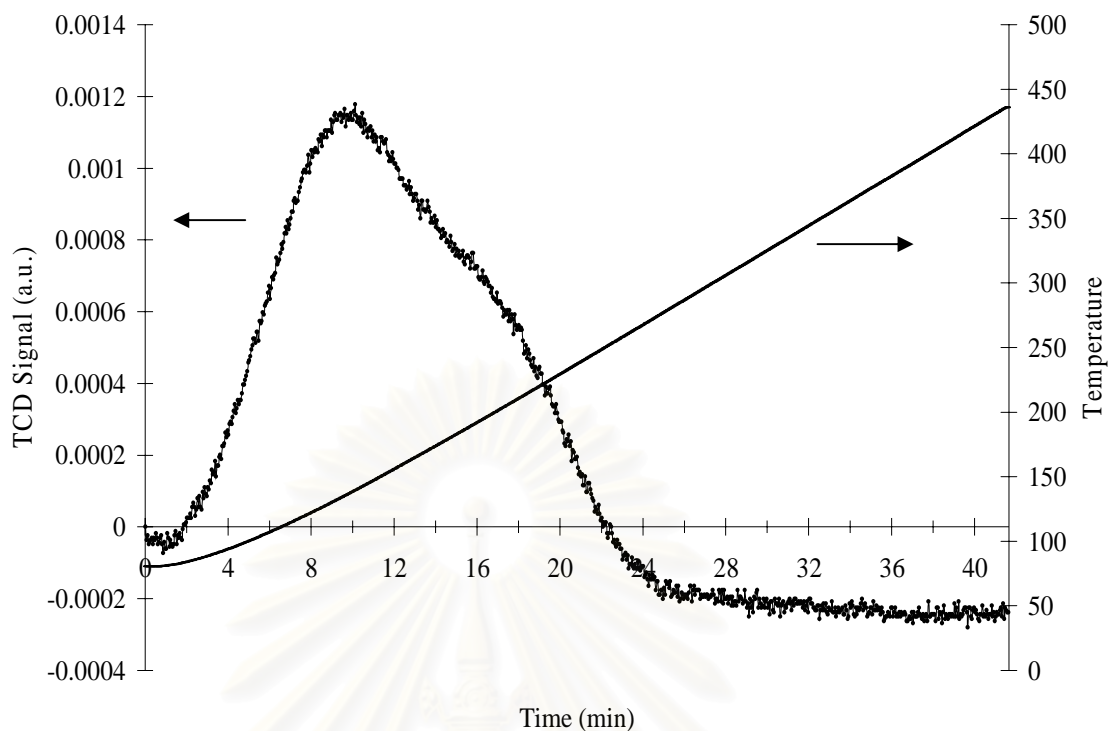
Figure 5.5 The relation of TCD signal and temperature versus time of the TS-1 before treatment.

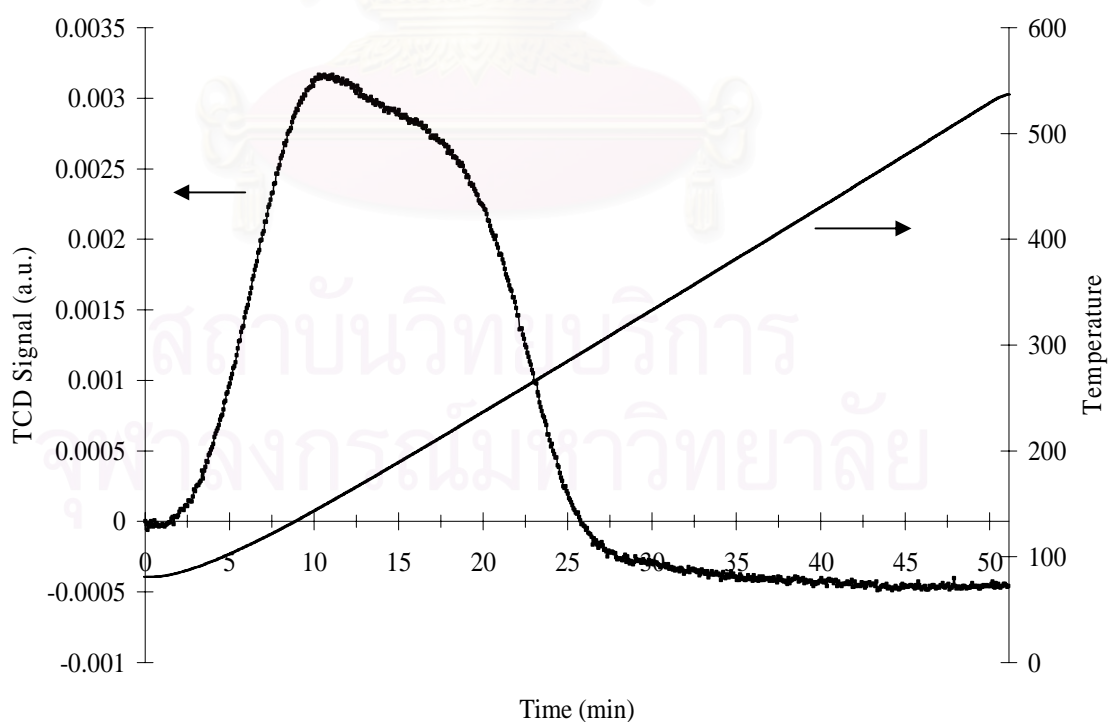**Figure 5.6** The relation of TCD signal and temperature versus time of the Co-TS-1 before treatment.
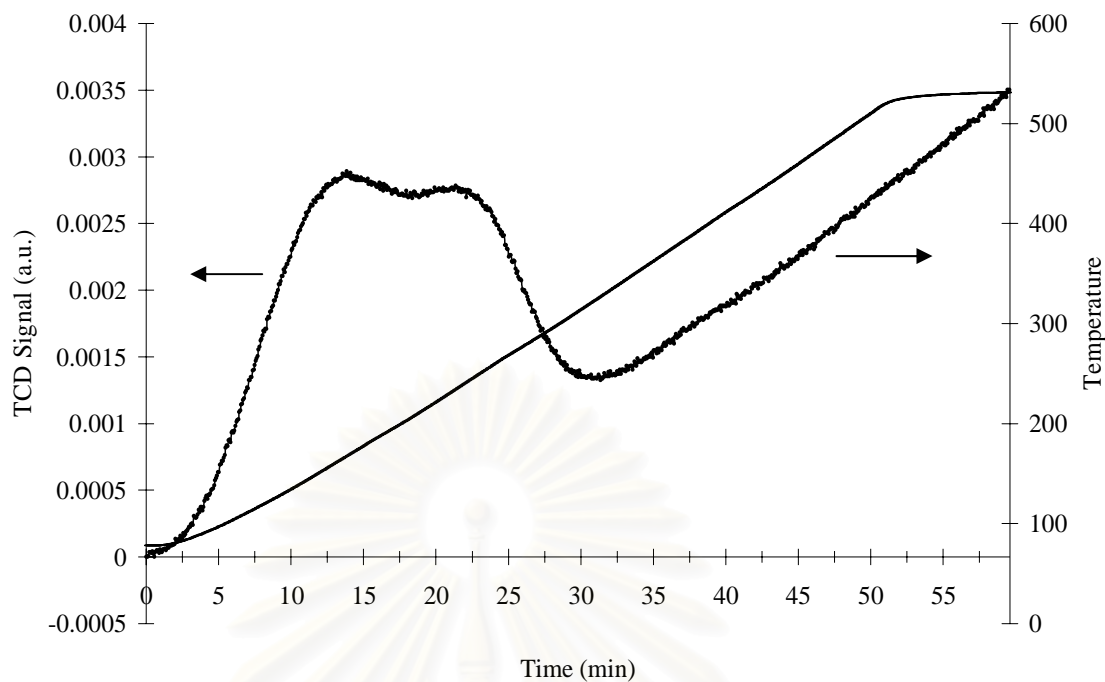
Figure 5.7 The relation of TCD signal and temperature versus time of the V-TS-1 before treatment.
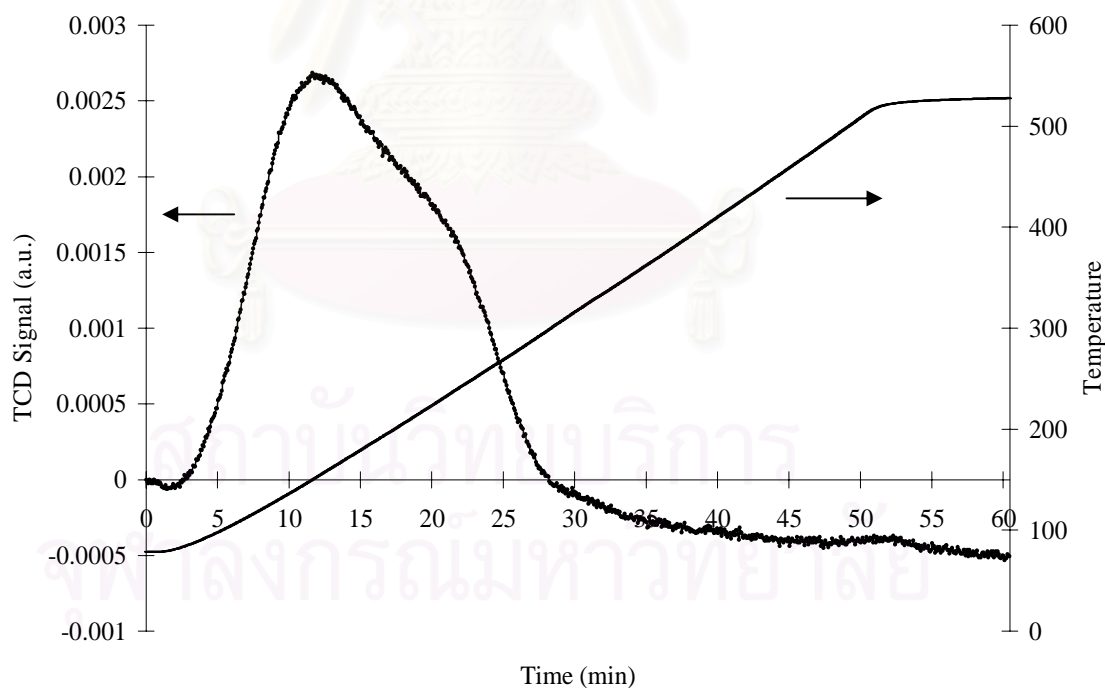

Figure 5.8 The relation of TCD signal and temperature versus time of the Fe-TS-1 before treatment.
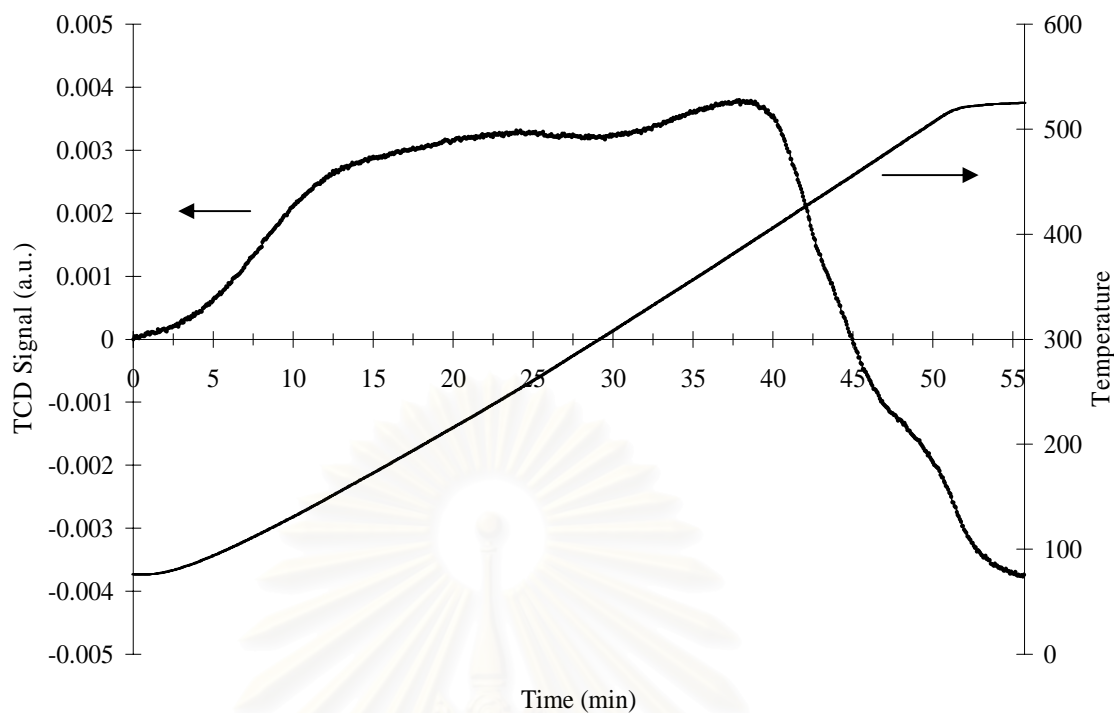
Figure 5.9 The relation of TCD signal and temperature versus time of the Al-TS-1 before treatment.

Figure 5.10 The data of peak fitting of TS-1 before treatment in table 5.3

Figure 5.11 The data of peak fitting of Co-TS-1 before treatment in table 5.

Figure 5.12 The data of peak fitting of V-TS-1 before treatment in table 5.3

Figure 5.13 The data of peak fitting of Fe-TS-1 before treatment in table 5.3

Figure 5.14 The data of peak fitting of Al-TS-1 before treatment in table 5.3
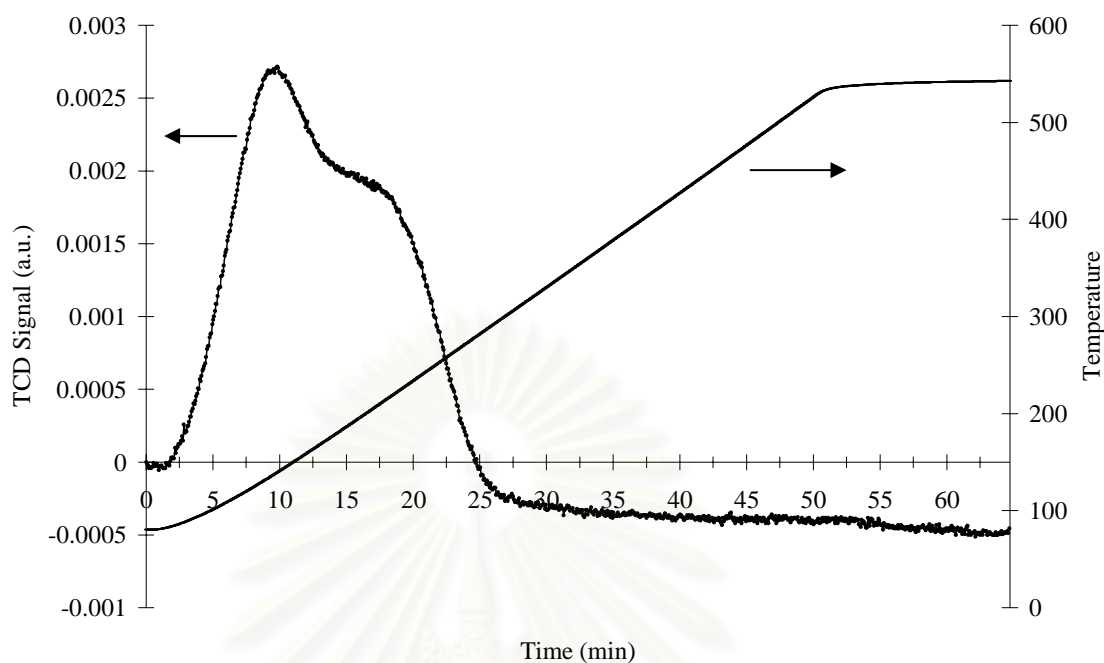
Figure 5.15 The relation of TCD signal and temperature versus time of the TS-1 after treatment.
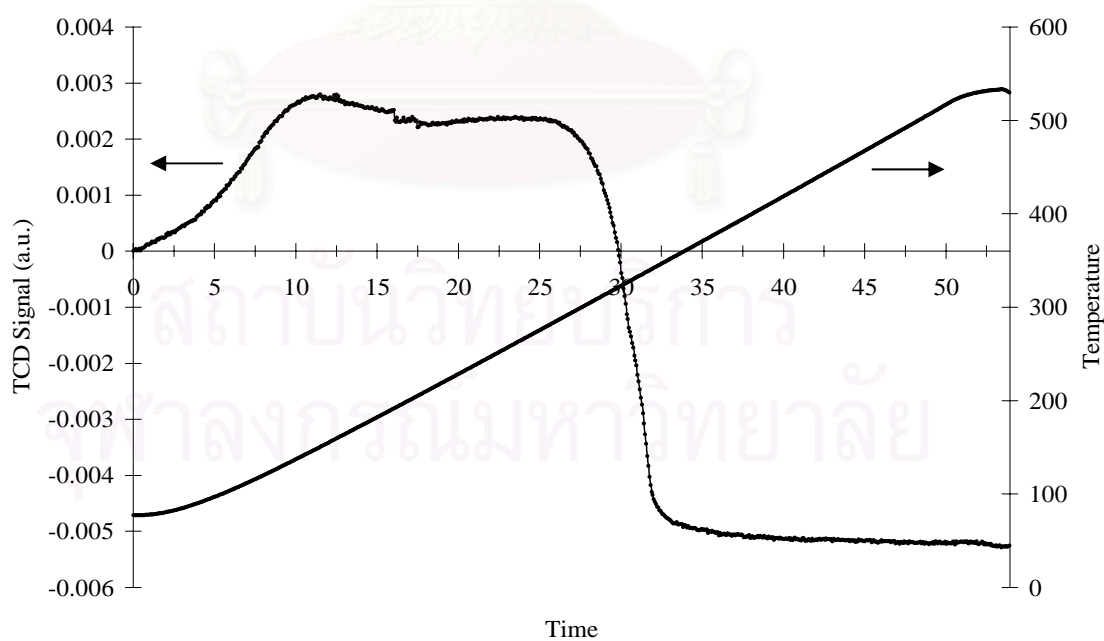
Figure 5.16 The relation of TCD signal and temperature versus time of the Co-TS-1 after treatment.
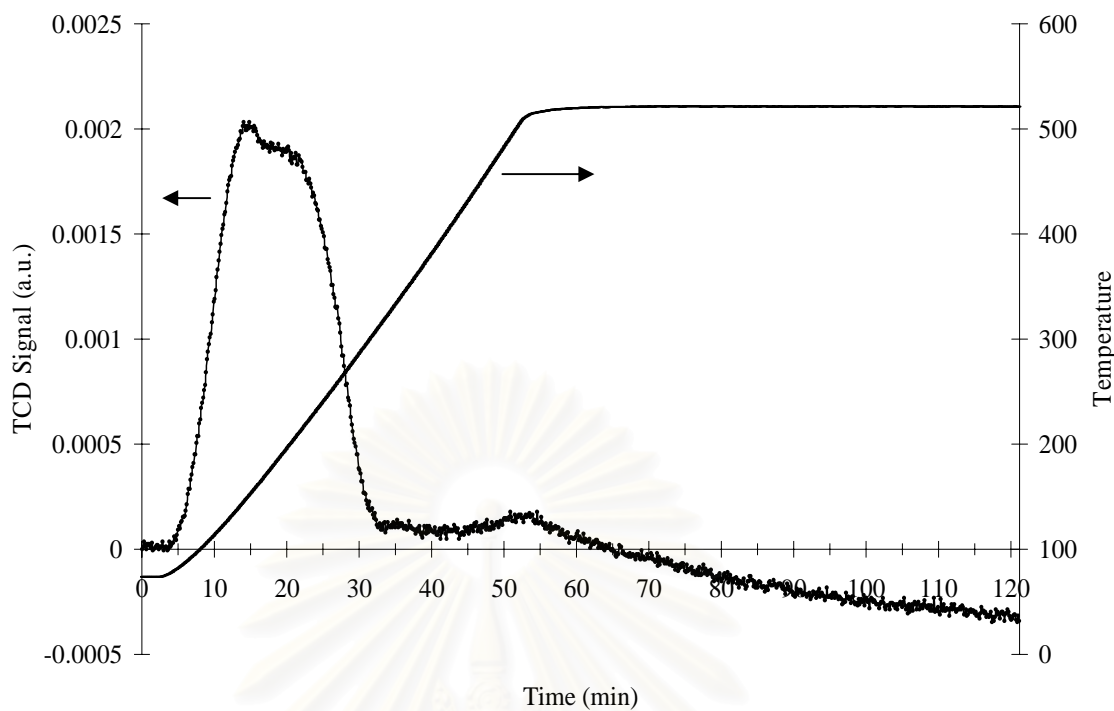
Figure 5.17 The relation of TCD signal and temperature versus time of the V-TS-1 after treatment.
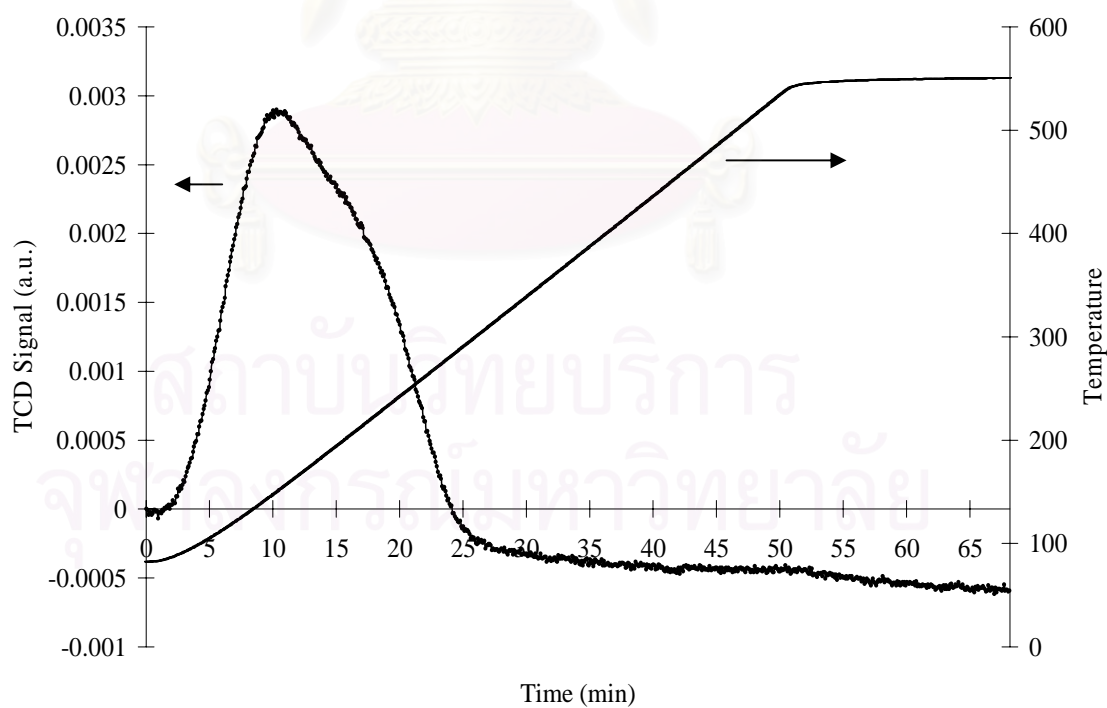
Figure 5.18 The relation of TCD signal and temperature versus time of the Fe-TS-1 after treatment.
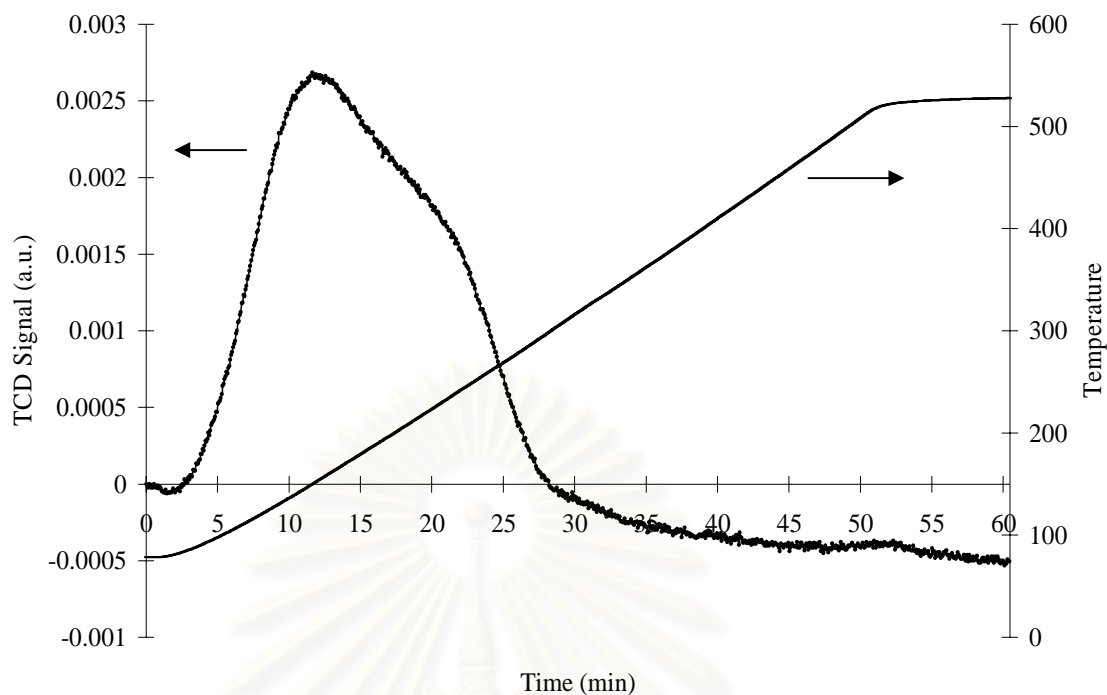
Figure 5.19 The relation of TCD signal and temperature versus time of the Al-TS-1 after treatment.
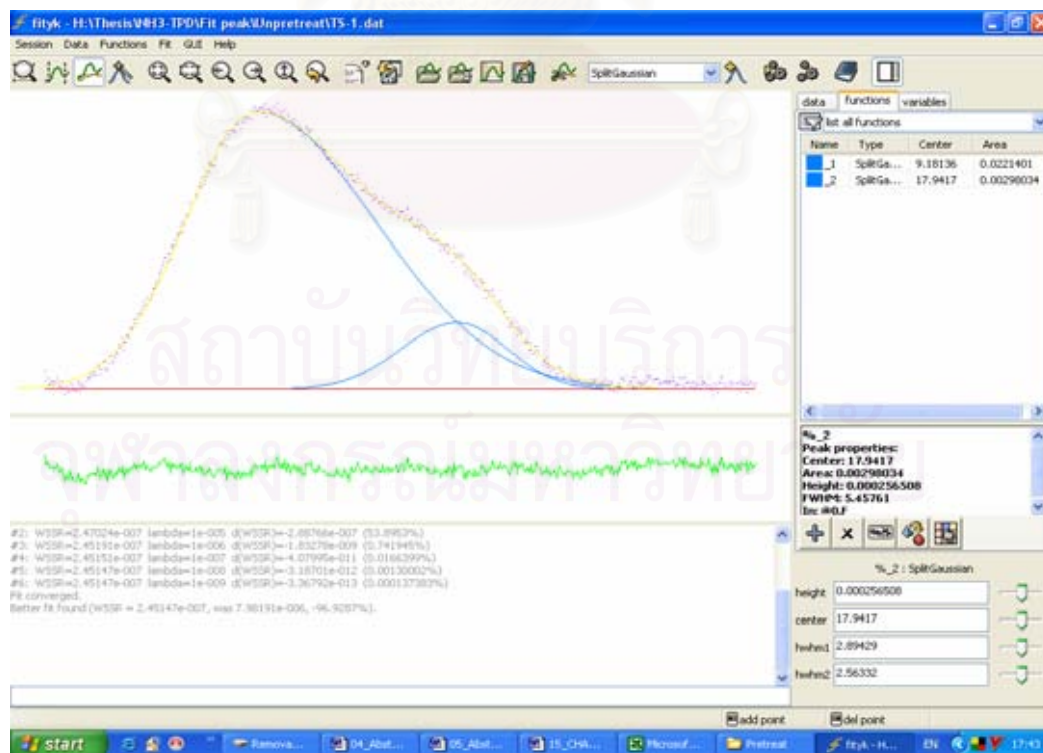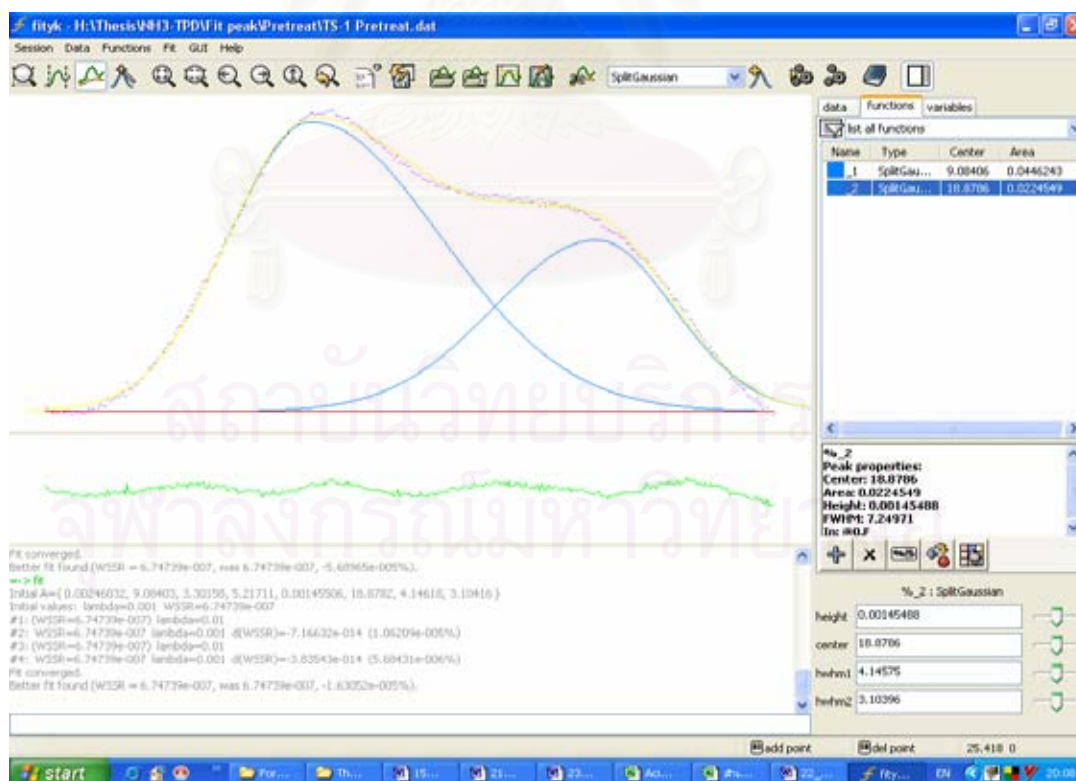

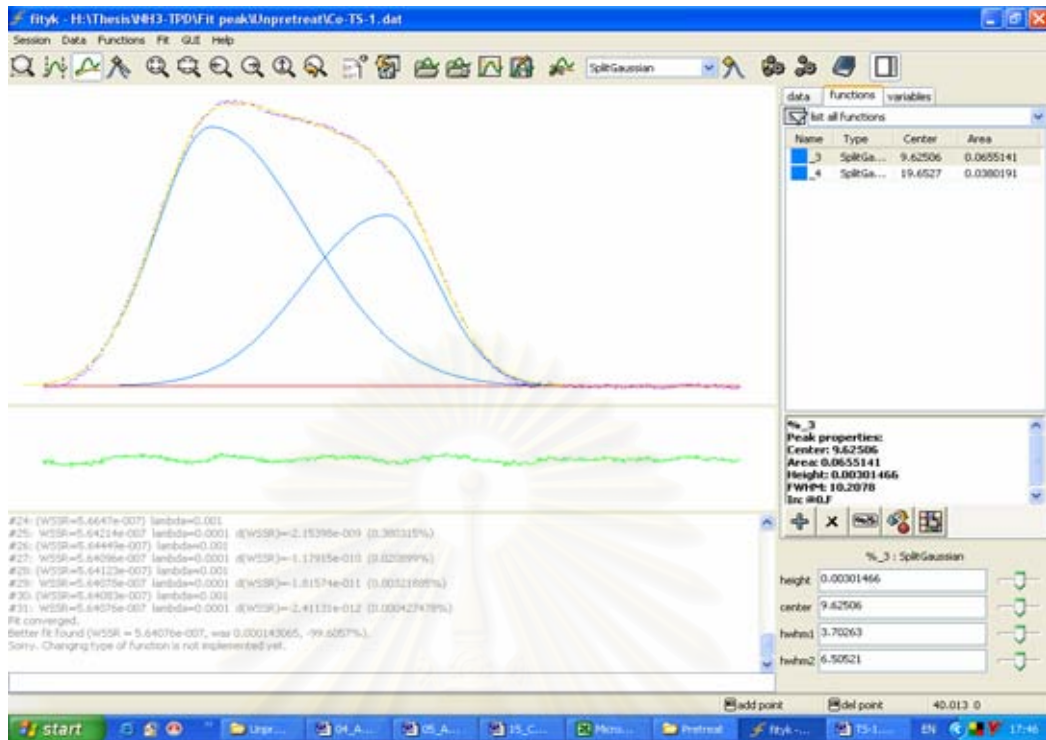**Figure 5.20** The data of peak fitting of TS-1 after treatment in table 5.3
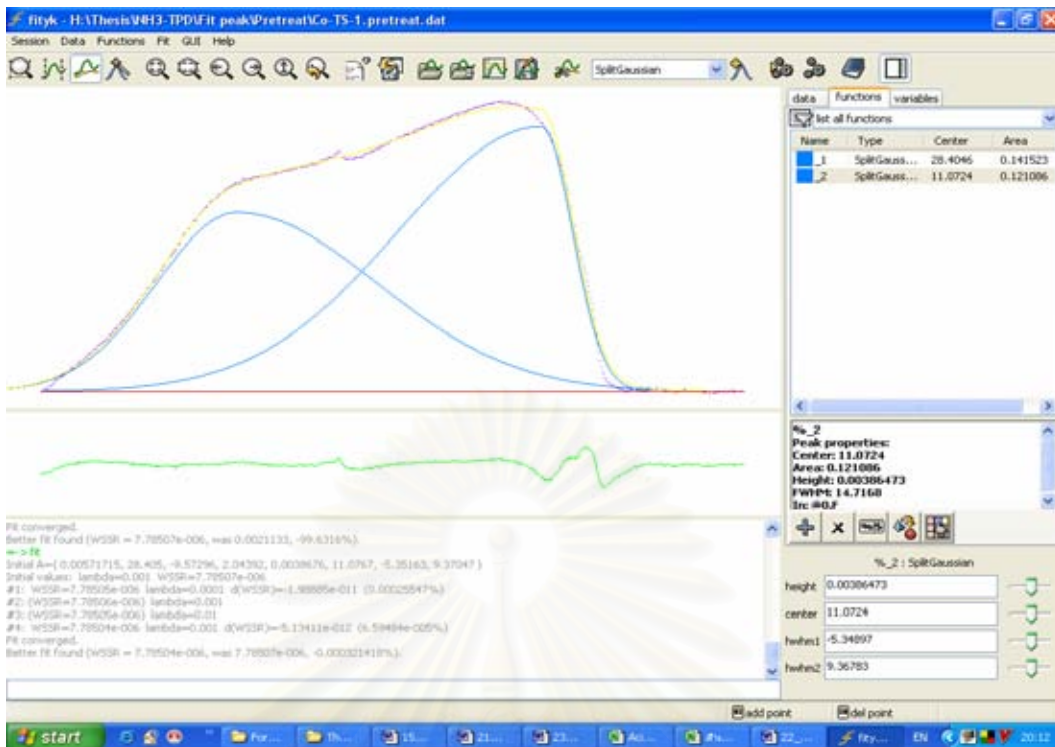
Figure 5.21 The data of peak fitting of Co-TS-1 after treatment in table 5.3
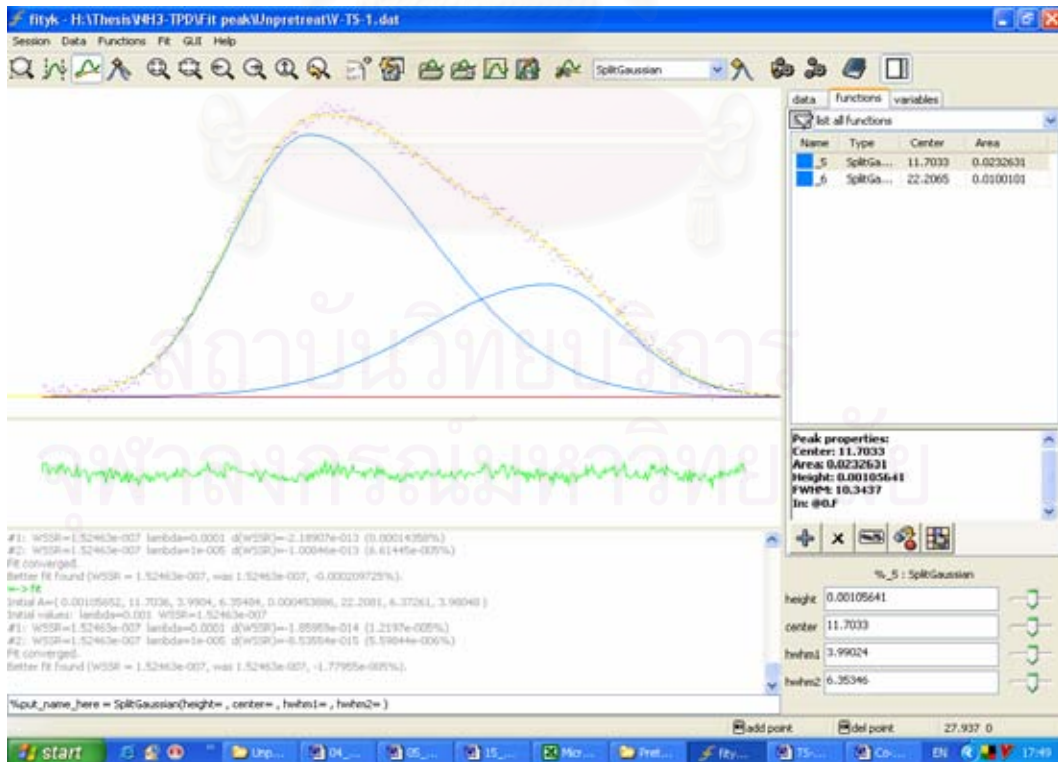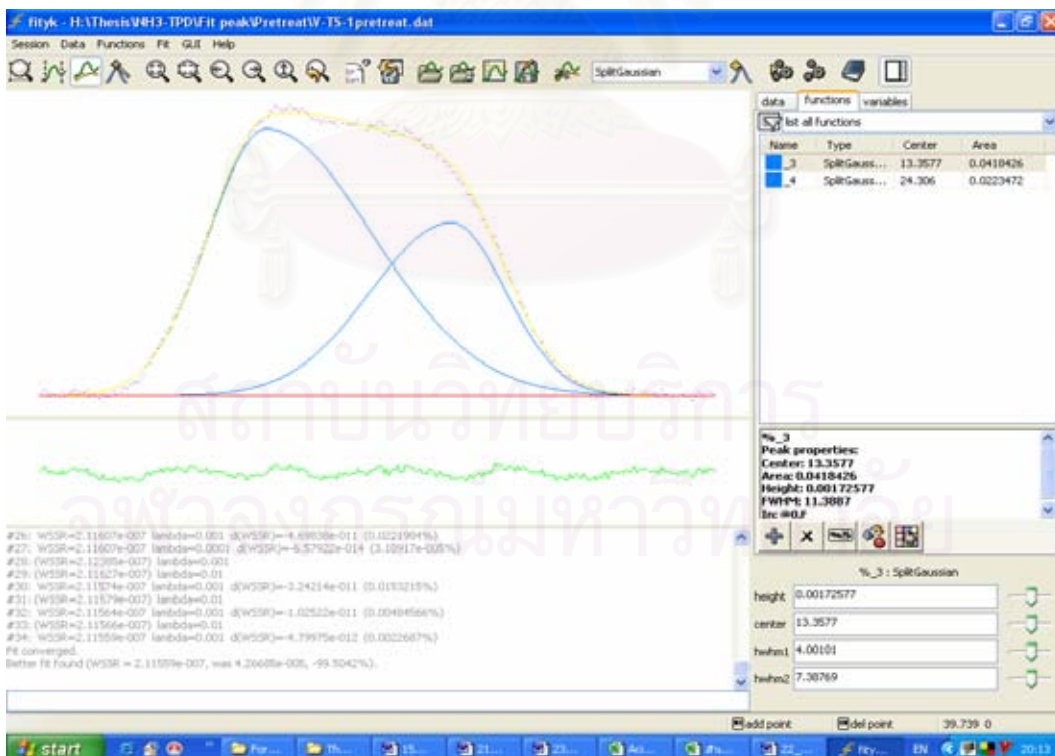

Figure 5.22 The data of peak fitting of V-TS-1 after treatment in table 5.3
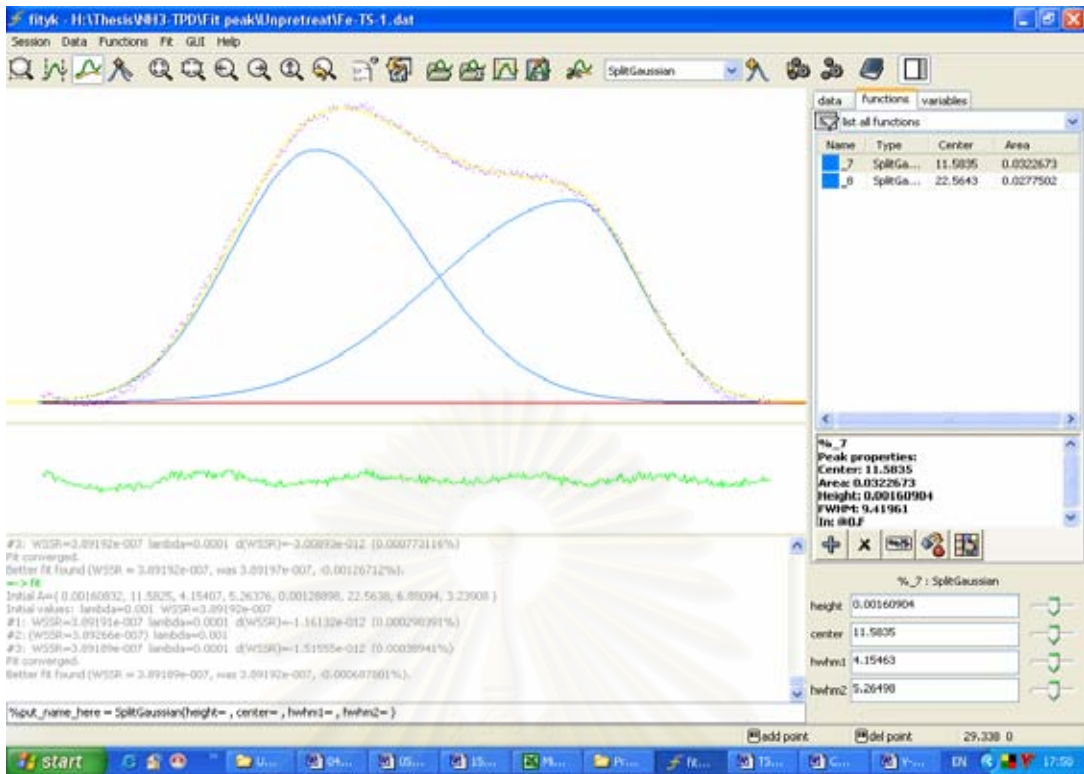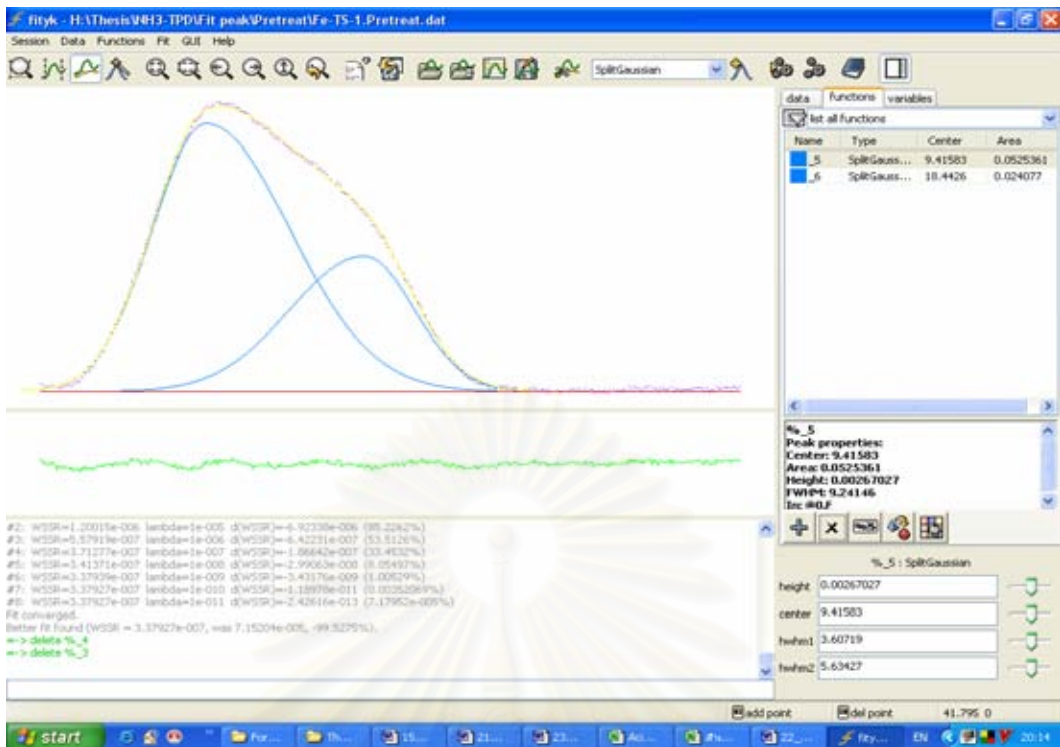
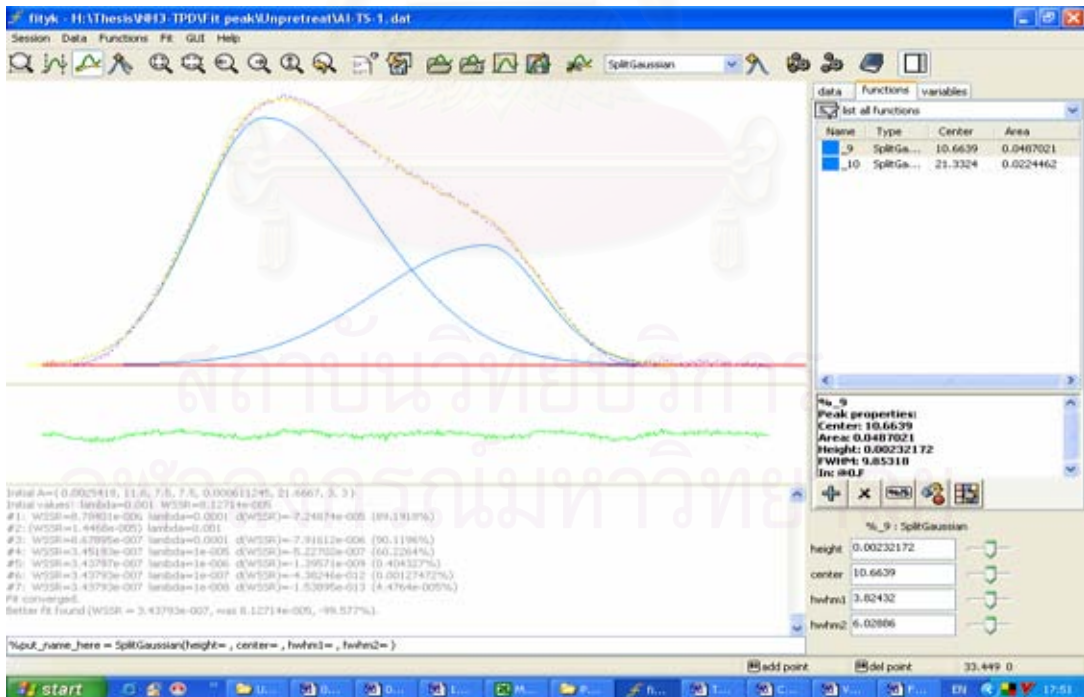**Figure 5.23** The data of peak fitting of Fe-TS-1 after treatment in table 5.3
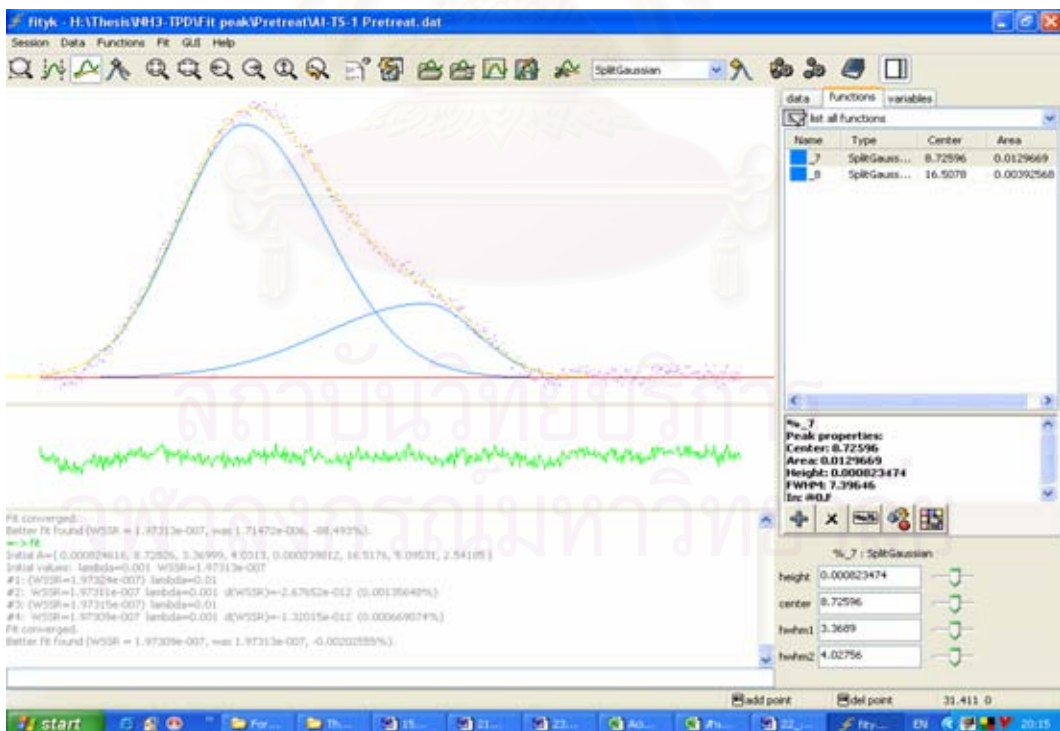
**Figure 5.24** The data of peak fitting of Al-TS-1 after treatment in table 5.3

Table 5.3 NH$_3$-TPD results

Sample	No pretreatment					With pretreatment				
	Weak acid site		Strong acid site		Total acid Site (μmol/g)	Weak acid site		Strong acid site		Total acid Site (μmol/g)
	Temp (°C)	Site (μmol/g)	Temp (°C)	Site (μmol/g)		Temp (°C)	Site (μmol/g)	Temp (°C)	Site (μmol/g)	
TS-1	127	132.9702	202	68.6091	201.5793	133	161.9265	224	77.4985	239.4249
Co-TS-1	138	197.9840	230	111.6636	309.6476	147	144.5241	308	169.6688	314.1929
V-TS-1	145	178.9808	234	95.5976	274.5716	141	107.4089	236	157.8859	265.2948
Fe-TS-1	149	133.5945	245	87.4348	221.0294	142	174.0403	227	112.8911	286.9314
Al-TS-1	141	167.3146	236	77.1132	244.4278	145	122.99885	242	93.7071	216.7056

5.2 Catalytic reaction

This section reports the hydroxylation activity of M-TS-1 and TS-1 catalysts without and with the pretreatment with 5M NHO_3 solution.

5.2.1 Effect of the second transition metal

The benzene hydroxylation results using TS-1, Co-TS-1, V-TS-1, Fe-TS-1, and Al-TS-1 at 70 °C for 3 hr are shown in the Figure 5.24. Typically, 1 g of a catalyst was reacted with 0.88 g of benzene and 1.27 g of aqueous H_2O_2 (benzene to H_2O_2 molar ratio equals to 1 to 1). It is found that the catalytic activity is in the following order Co-TS-1 > V-TS-1 > Fe-TS-1 > Al-TS-1 > TS-1. The maximum benzene conversion was achieved with Co-TS-1 about 9.85 %.
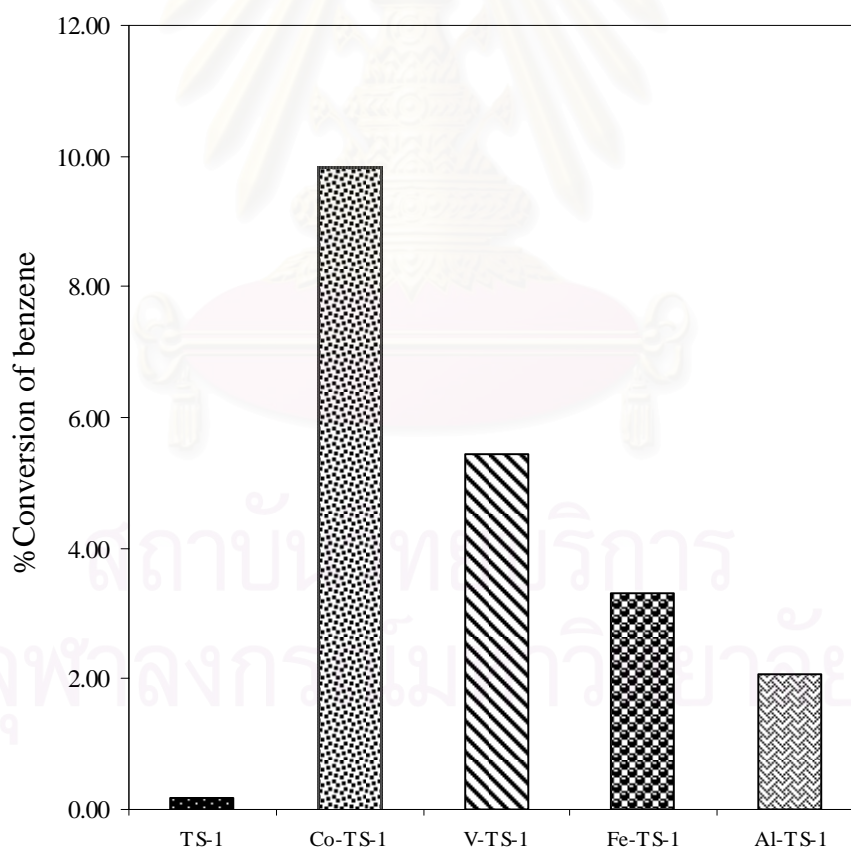
Figure 5.25 The hydroxylation of benzene with H_2O_2 using TS-1, Co-TS-1, V-TS-1, Fe-TS-1, and Al-TS-1.

The acid strength of M-TS-1 catalysts more than TS-1 catalyst. The NH_3-TPD data (Table 5.3) indicated that the metal including Co, V, Fe, and Al incorporated in TS-1 framework increased the acid strength of the catalyst. The acid strength of catalysts were decreased in the order Co-TS-1 > V-TS-1 > Fe-TS-1 > Al-TS-1 > TS-1. The role of surface acidity on the hydroxylation acidity later in section.5.2.5.

5.2.2 Effect of pretreatment

From section 5.2.2, the catalysts would be pretreated with 5M HNO_3 solution and used for the hydroxylation of benzene. The hydroxylation activities of the catalysts without any pretreatment, pretreated with 5M HNO_3 are compared in Figure 5.25.

The experimental results in Figure 5.17 indicate the benzene conversions of catalysts are pretreated with 5M HNO_3 are higher than that of the unpretreat catalyst. The benzene conversion of the catalyst pretreated with 5M HNO_3 decreased in the order Co-TS-1 > V-TS-1 > Fe-TS-1 > Al-TS-1 > TS-1. This is the reason why the catalysts before pretreatment, exhibits lower benzene conversion than the catalysts after pretreatment. When the inactive structure can be better removed by washing with HNO_3 solution. In addition, TiO_2 in framework was decreased (Table5.1) [Liu et al. (2004)], they found that the TS-1 framework structure was not destroyed and titanium in the framework was not removed and its surface area changed hardly, but some extra-framework TiO_2 could be removed partly, which led to the slight increase of the crystalline of catalyst. Therefore, the catalysts washed with HNO_3 solution performed high activity, the conversion of benzene increases. It is recommended to wash the catalyst by using HNO_3 solution before performing the hydroxylation of benzene in any future works that may occur.
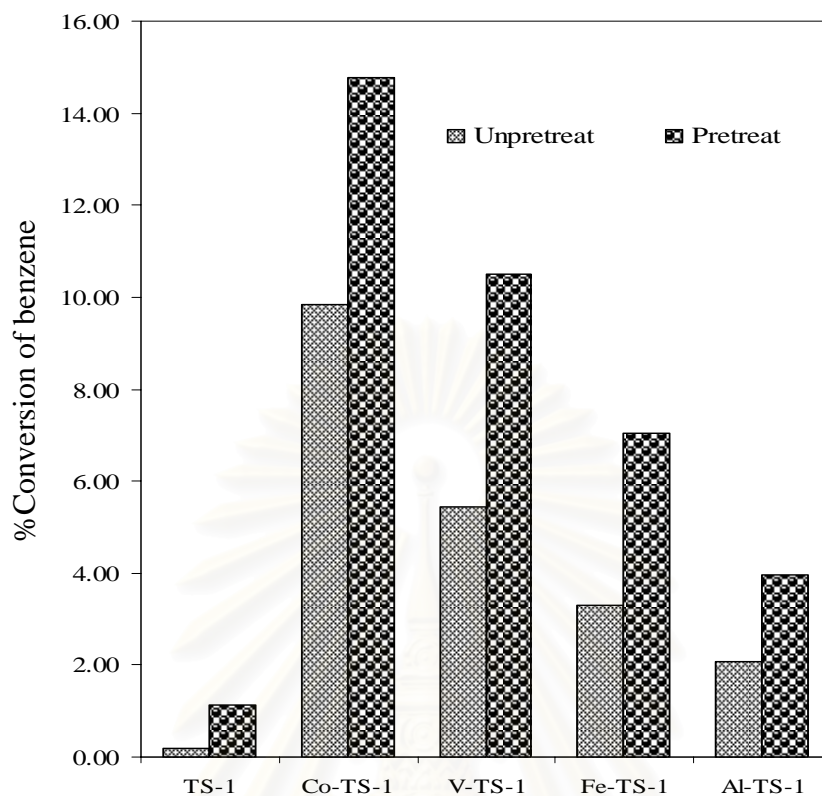
Figure 5.26 The effect of before and after treatment of catalysts

5.2.3 Effect of temperature

In Figures 5.26, and 5.27, the effect of temperature on the phenol productivity in the hydroxylation of benzene is shown. Upon increasing the temperature from 50 ^{o}C to 70 ^{o}C, the rate of reaction increases with the formation of phenol produce, as expected. Very low phenol produce was observed at 80 ^{o}C. The optimum reaction temperature, under the present conditions, was fond to be 70 ^{o}C. Hence, all other experiments were carried out at 70 ^{o}C.
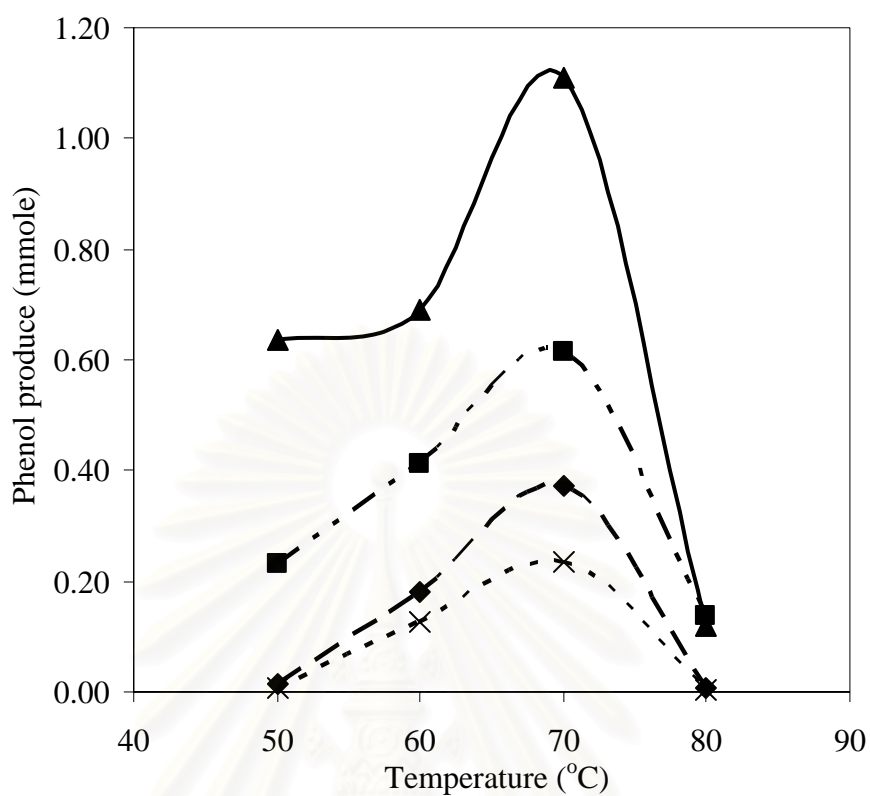
Figure 5.27 The effect of temperature using before treatment of Co-TS-1(▲), V-TS-1 (■), Fe-TS-1(♦), and Al-TS-1(×) catalysts.
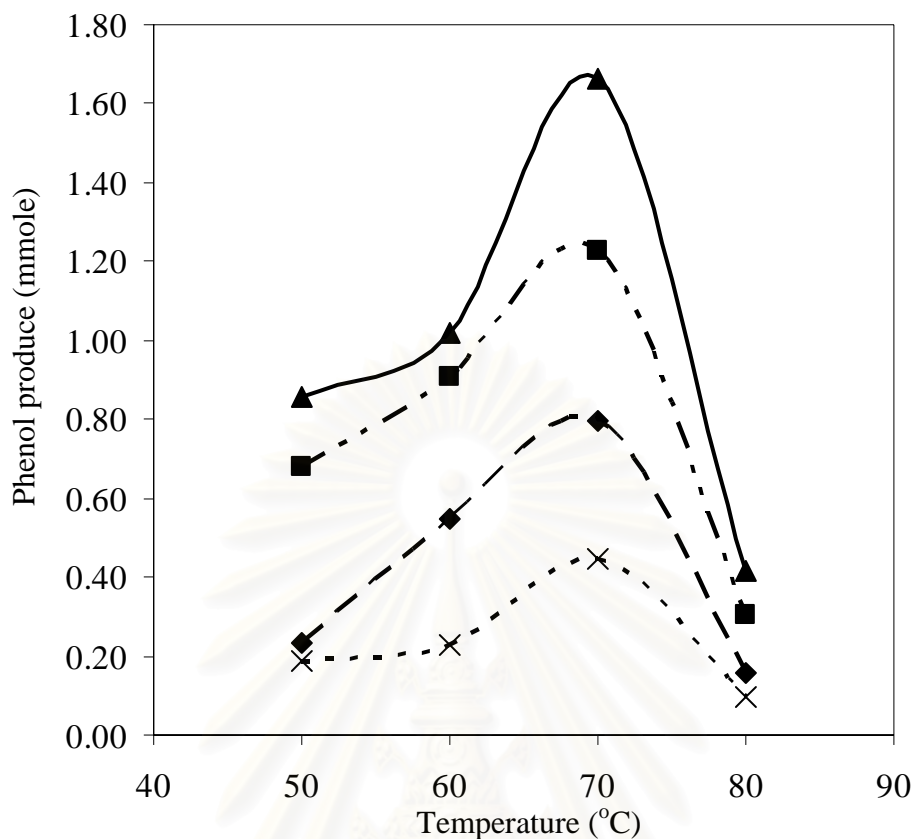
Figure 5.28 The effect of temperature using after treatment of Co-TS-1(▲), V-TS-1 (■), Fe-TS-1(♦), and Al-TS-1(×) catalysts.

5.2.4   Effect of benzene/H_2O_2 molar ratio

In Figures 5.28, and 5.29, the effect of the substrate to H_2O_2 molar ratio in the hydroxylation of benzene over before and after treatment catalysts is reported. With increasing benzene/H_2O_2 molar ratio, both before and after treatment catalysts the formation of phenol produce were also increased, as expected. However, the rate of reaction increase by increasing benzene to H_2O_2 molar ratio. In all other experiments were carried out at 1 to 1 of benzene/H_2O_2 molar ratio.
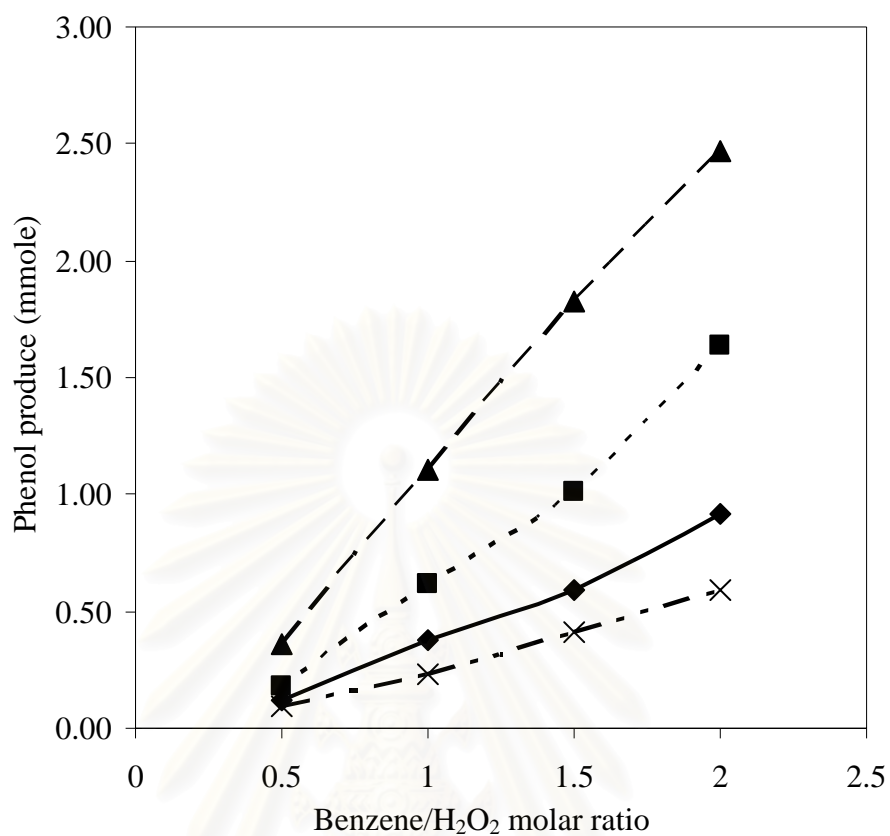
Figure 5.29 The effect of benzene/H$_2$O$_2$ molar ratio using before treatment of Co-TS-1(▲), V-TS-1 (■), Fe-TS-1(♦), and Al-TS-1(×) catalysts.
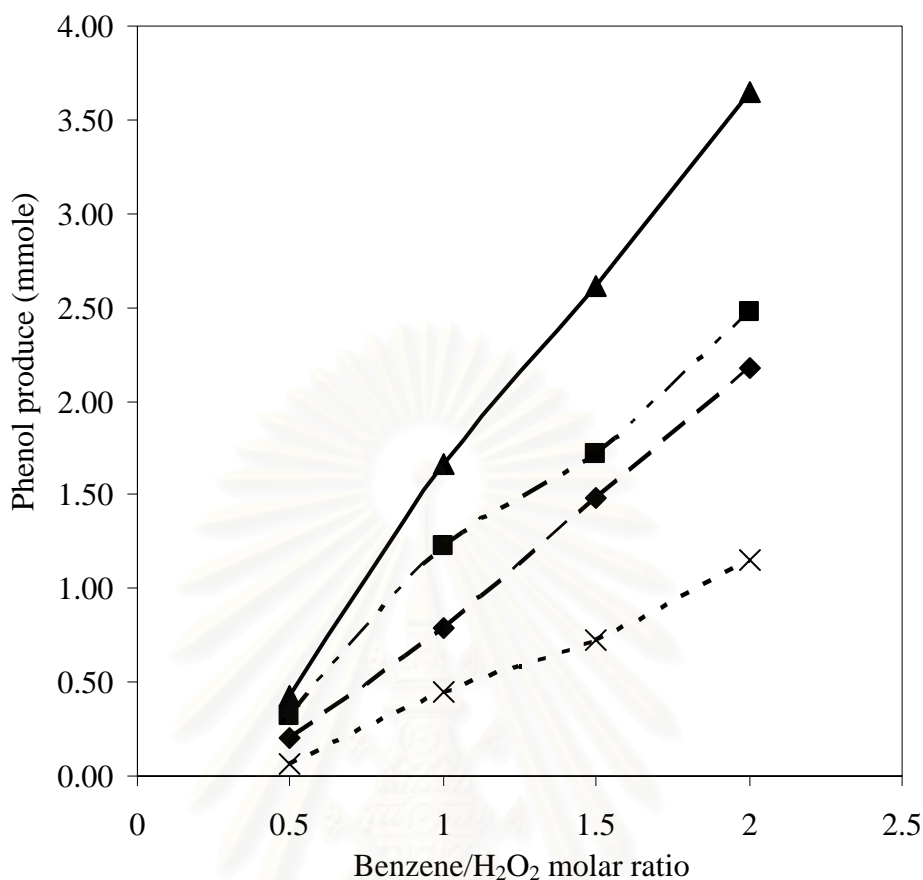
Figure 5.30 The effect of benzene/H_2O_2 molar ratio using after treatment of Co-TS-1(▲), V-TS-1 (■), Fe-TS-1(♦), and Al-TS-1(×) catalysts.

5.2.5 Effect of reaction time

The catalytic behavior of catalyst without pretreatment and with pretreatment are compare in Figures 5.30, and 5.31, respectively. As a measure for the catalytic activity of catalysts, the phenol produce was chosen. It can be seen from Figures 5.22, and 5.23 that there was a steady increase in the phenol produce with an increase of times. The rate of hydroxylation is somewhat lower for Al-TS-1 catalyst. And the rate of hydroxylation is the highest for Co-TS-1 catalyst.
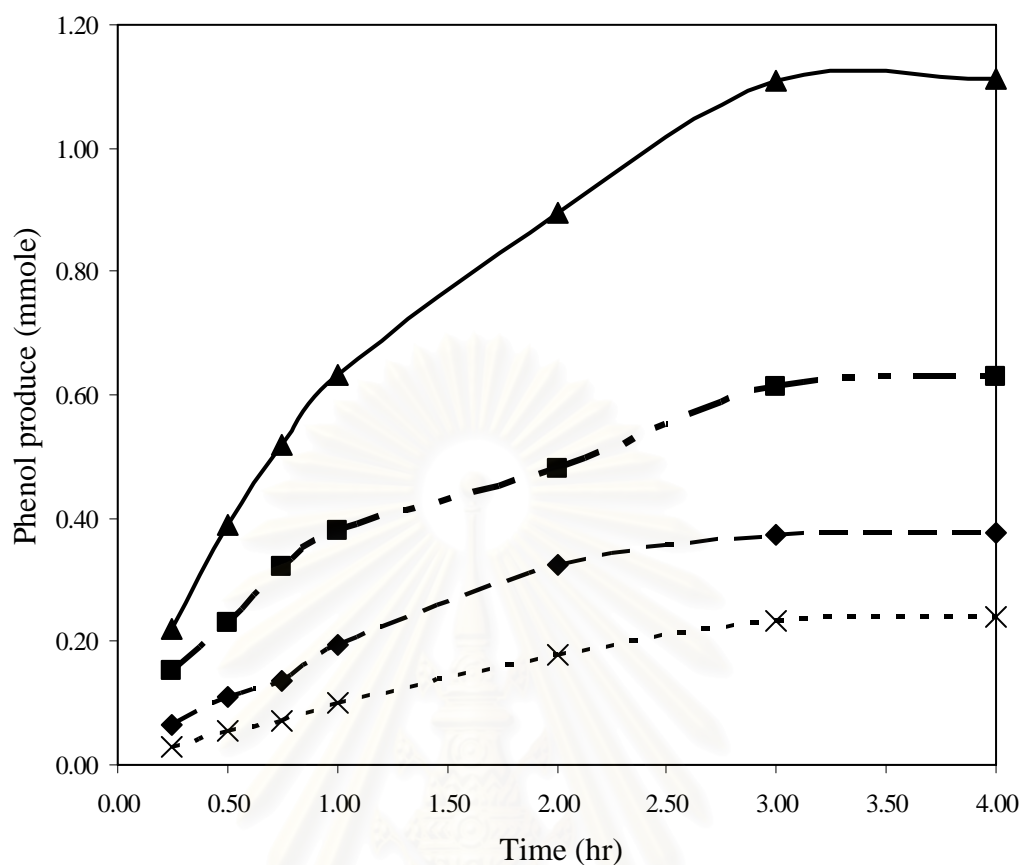
Figure 5.31 The effect of reaction time using before treatment of Co-TS-1(▲), V-TS-1 (■), Fe-TS-1(♦), and Al-TS-1(×) catalysts.
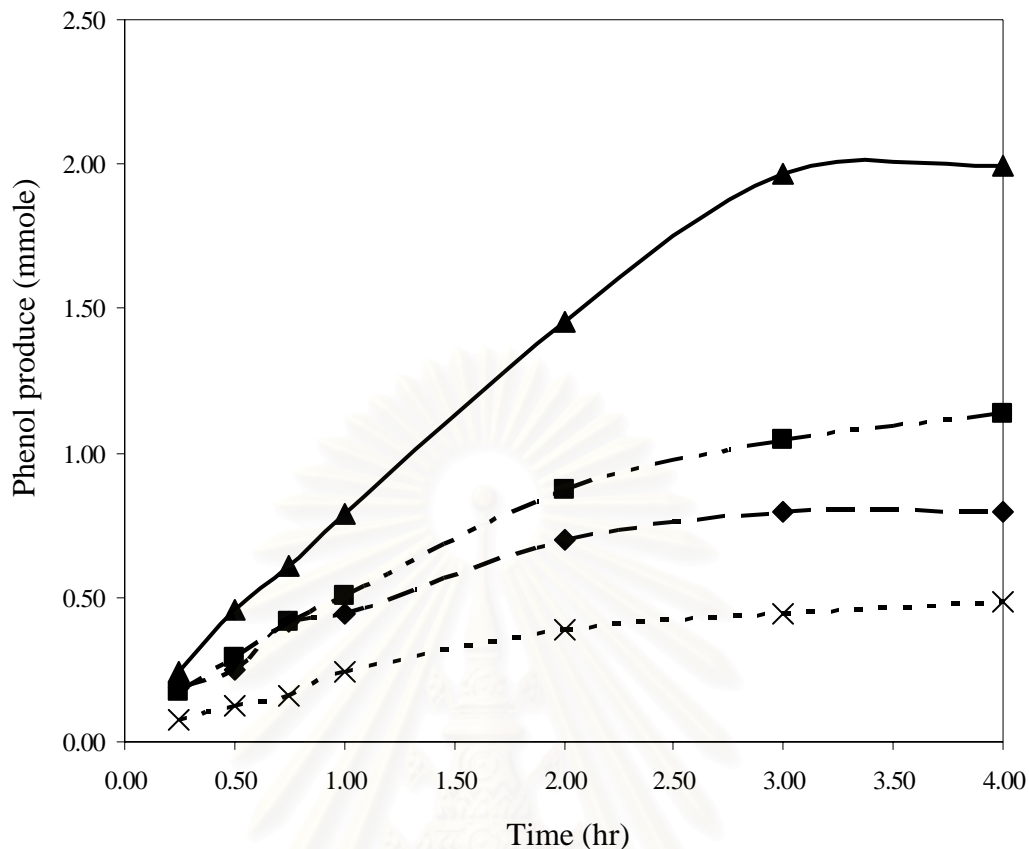
Figure 5.32 The effect of reaction time using after treatment of Co-TS-1(▲), V-TS-1 (■), Fe-TS-1(♦), and Al-TS-1(×) catalysts.

It is known that some metal cation can accelerate the decomposition rate of H_2O_2. In additional, the colour of the catalysts changed after the reaction, indicating that there are some species deposited on the catalyst surface. These two phenomenon may be the causes that causes the phenol productivities dropped to different level, depending on the catalyst used. To prove these hypothesis, two additional experiments were set up. The first one is to determine the amount of H_2O_2 remained after the catalysts were put in. The second one is to determine the amount of phenol remained in the solution after the catalyst were put in.

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To quantity the decomposition of H_2O_2, a solution of $KMnO_4$ is used to measured amount of H_2O_2. In the experiments, 1 g of catalyst with 1.27 g of aqueous H_2O_2 (1 ml) is mixed at 70 $^{\circ}$C for 3 hr and then titrate with the standard $KMnO_4$ solution. The titration is carried out until the colour of the solution became purple (all H_2O_2 was consumed). The volume of $KMnO_4$ solution used directly varied with the

amount of H_2O_2 remained. The results are shown in the Figure 5.32. It is found that the decomposition of H_2O_2 is in the following order Co-TS-1 < V-TS-1 < Fe-TS-1 < Al-TS-1 < TS-1. The Co-TS-1 has the highest amount of H_2O_2 remained. Therefore, the catalytic activity of the system using Co-TS-1 is the best.

A possible mechanism to explain the role of the decomposition of H_2O_2 are shown in the Figure 5.33. An important step in the above scheme is the regeneration of the active site (from Ti-OH to Ti-O-O-H) by oxygen atom from the decomposition of H_2O_2. However, not all the oxygen occurred from the decomposition of H_2O_2 can react with Ti-O-H site to produce the active Ti-O-O-H species, they may react with each other to from O_2 which contributes no role in the reaction.
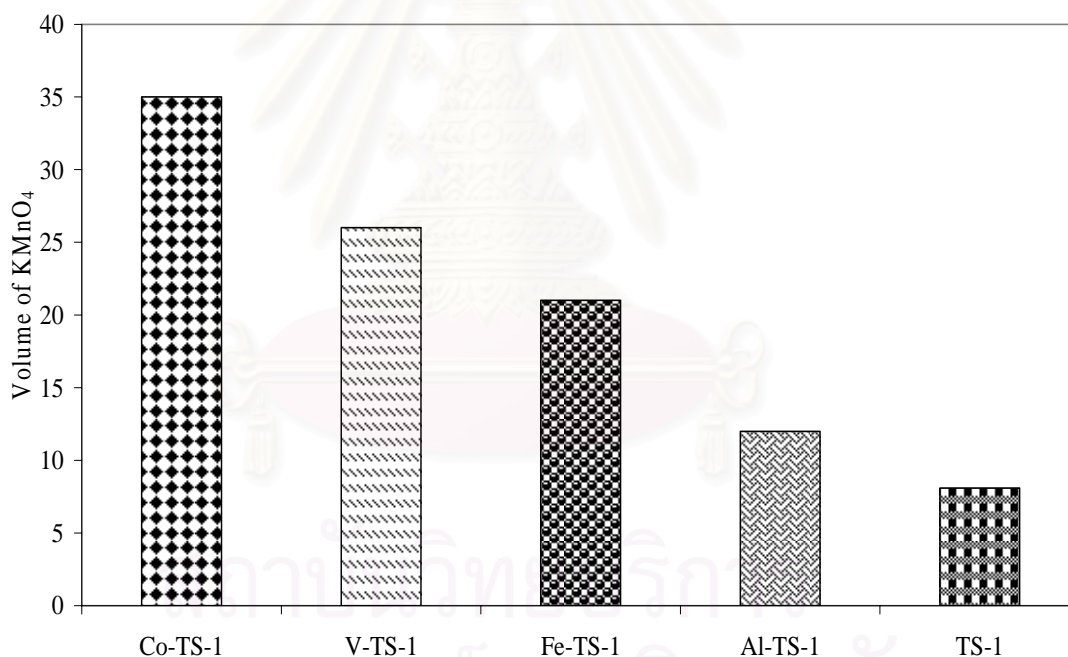
Figure 5.33 The titration of hydrogen peroxide solutions with standardize $KMnO_4$
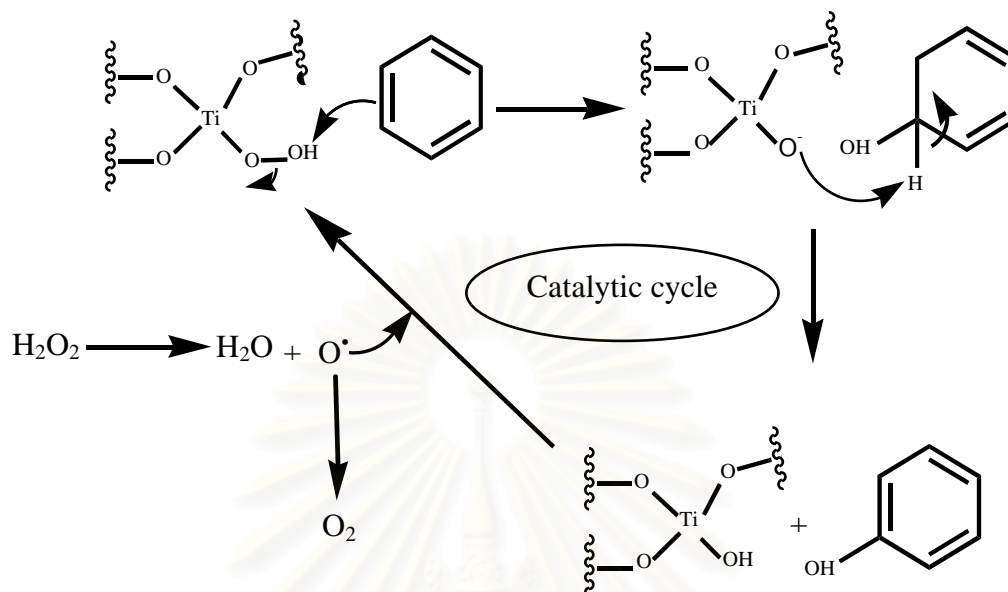
Figure 5.34 The reaction pathway of the hydroxylation of benzene by H_2O_2 over TS-1 catalyst (Modified from Notari, 1989)

To determine the phenol adsorption capacities of the catalyst, a phenol solution is prepared and divide in to 5 tube is blank, added with Co-TS-1, V-TS-1, Fe-TS-1, Al-TS-1 and TS-1. The concentrations of phenol remained in the solution were measured at 3 and 11 hours. The results are shown in Figure 5.34. The graphs shown the phenol solution which has Co-TS-1 has the highest number of active site available for the reaction. On the other hand, the phenol solution which has TS-1 has the lowest and, indications that this catalyst preferred the adsorption of phenol. This result explained why the TS-1 has the lowest catalytic activity for the hydroxylation of benzene.
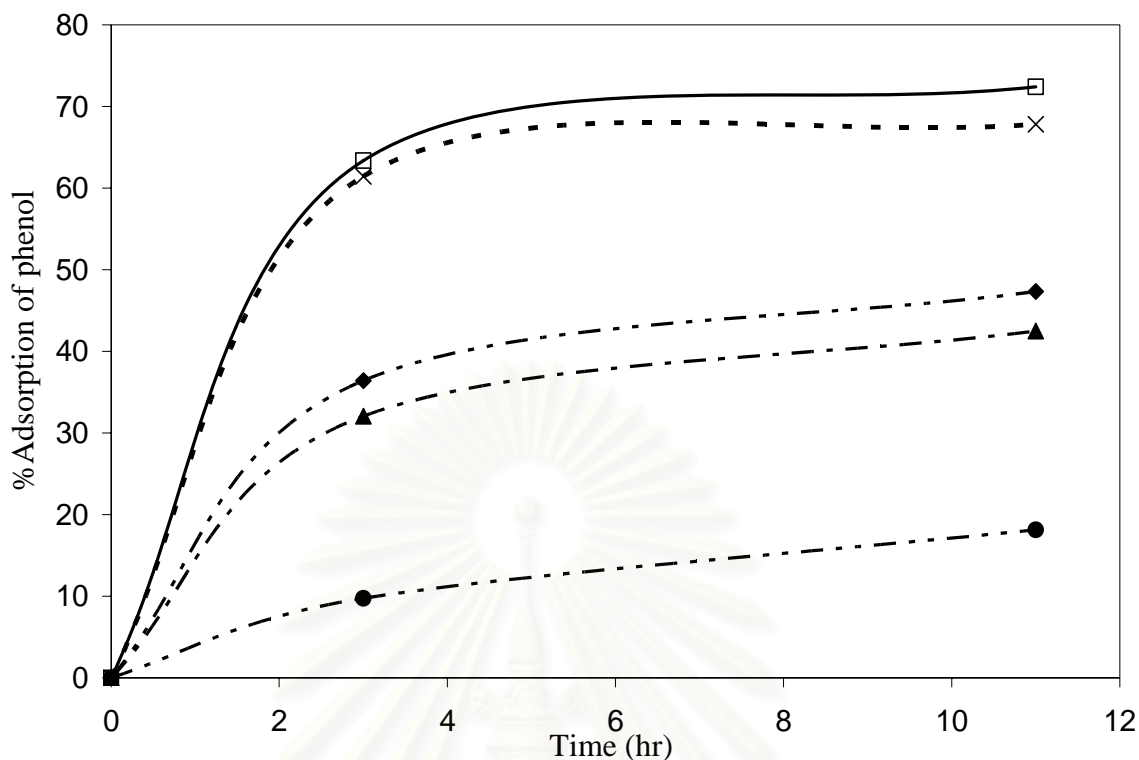
Figure 5.35 The adsorption of phenol of Co-TS-1(●), V-TS-1 (▲), Fe-TS-1(♦), Al-TS-1(×) and TS-1(□) catalysts.

The results in section 5.2.1, already the acidity of the surface is in the following sequence Co-TS-1 > V-TS-1 > Fe-TS-1 > Al-TS-1 > TS-1. The high acidity of the Co-TS-1 presents the adsorption of phenol (an acidic compound) on the catalyst surface. The less phenol deposits on the catalyst surface, the more active site available for the reaction.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATION

In the present research, the catalytic activity of TS-1 catalysts modified by Fe, Al, Co, and V were synthesized and of pretreatment with 5M HNO_3 solution in the hydroxylation of benzene by H_2O_2. The conclusions emerged from all the experiments are summarized in section 6.1. In addition, recommendations for further study are given in section 6.2.

6.1 Conclusions

1. The catalytic activity is in the following order Co-TS-1 > V-TS-1 > Fe-TS-1 > Al-TS-1 > TS-1. The maximum benzene conversion was achieved with Co-TS-1 about 9.85 %.

2. The benzene conversions of catalysts are pretreated with 5M HNO_3 are higher than that of the without pretreatment catalyst. The benzene conversion of the catalyst pretreated with 5M HNO_3 decreased in the order Co-TS-1 > V-TS-1 > Fe-TS-1 > Al-TS-1 > TS-1. When the inactive structure can be better removed by washing with 5M HNO_3 solution. Therefore, the catalysts washed with HNO_3 solution performed high activity, the conversion of benzene increase.

3. There are two reasons that causes the phenol productivities dropped to different level, depending on the catalyst used. The first one is the decomposition of H_2O_2. And the second one is the phenol adsorption of the catalyst. The Co-TS-1 has the highest amount of H_2O_2 remained and number of active site available for the reaction. Therefore, the catalytic activity is the best.

6.2 Recommendations

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

1. Other choices of method for synthesized catalysts including sources of Si, Ti and the metal template and base solution should be further investigated.

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

3. Other operation should be by changing the reactor and phase reaction such as gas-solid-liquid phase should also be manipulated to find an optimal operating condition.

4. Should be study to leaching of cation such as Si and Ti.

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APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

The calculation is based on weight of Sodium Silicalite ($Na_2O \cdot SiO_2 \cdot H_2O$) in B1 and B2 solutions (Topic 4.1.2).

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

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

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

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

$$= \quad 0.3273$$

MFI catalyst

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

Molecular weight of Ti	=	47.88
Molecular weight of $Ti[O(CH_2)_3CH_3]_4$	=	340.36
Weight % purities of $Ti[O(CH_2)_3CH_3]_4$	=	97

Si/Ti atomic ratio = 50

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

$$= 6.546 \times 10^{-3} \text{ mole}$$

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

$$= 2.2970 \text{ g}$$

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.
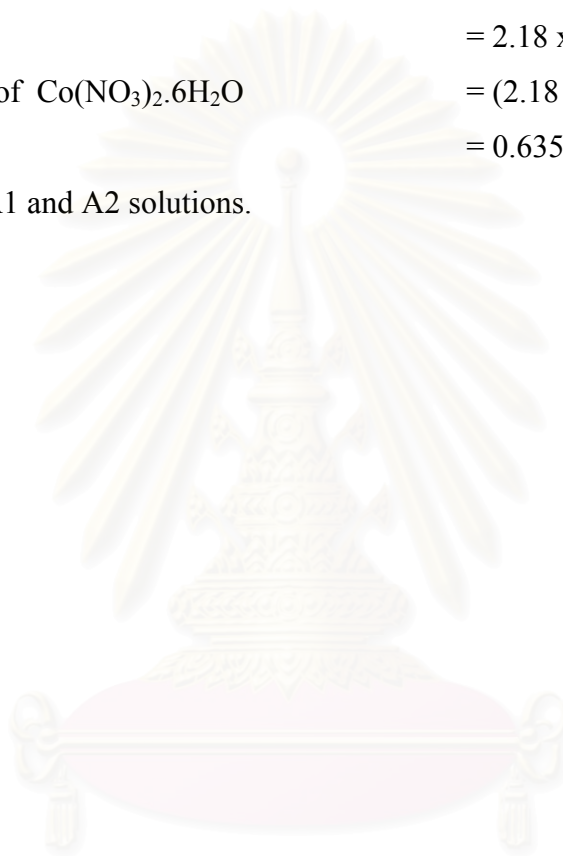
APPENDIX B

DATA AND CALCULATION OF ACID SITE

Table B1 Reported total peak area from Micromeritrics Chemisorb 2750

No pretreatment		With pretreatment	
Sample	Reported total peak area	Sample	Reported total peak area
TS-1	0.0246	TS-1	0.0741
Co-TS-1	0.1040	Co-TS-1	0.2621
V-TS-1	0.0642	V-TS-1	0.0742
Fe-TS-1	0.0748	Fe-TS-1	0.0866
Al-TS-1	0.0711	Al-TS-1	0.2290

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

$$\text{Total peak volume} = 77.5016 \times \text{total peak area}$$
$$= 77.5016 \times 0.0246$$
$$= 1.9065 \text{ ml}$$

2. Calculation for adsorbed volume of 15% NH_3

$$
\begin{aligned}
\text{adsorbed volume of 15\% } NH_3 \quad &= 0.15 \times \text{total peak volume} \\
&= 0.15 \times 1.9065 \ ml \\
&= 0.2860 \ ml
\end{aligned}
$$

3. Total acid sties are calculated from the following equation

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

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

$$
\text{Total acid sites} = \frac{0.2860 \, \text{ml} \times 101.325 \, \text{Pa}}{\left(8.314 \times 10^{-3} \dfrac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}}\right) \times 298 \, \text{K} \times (0.1005 \, \text{g})}
$$

$$
= 201.5793 \ \mu\text{mol H}^+/\text{g}
$$

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 Fig. 5.14., 1st peak area and 2nd peak area are equal to 0.0162 and 0.0084, respectively.

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

$= 65.96\ \%$

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

$= 34.04\ \%$

APPENDIX C

CALIBRATION CURVES

This appendix shows the calibration curves for calculation of composition of reactant and products in hydroxylation of benzene reaction. The reactant is benzene and the main product is phenol.

The flame ionization detector, gas chromatography Shimadzu model 9A was used to analyze the concentration of benzene and 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 curve of phenol is illustrated in the following figure.
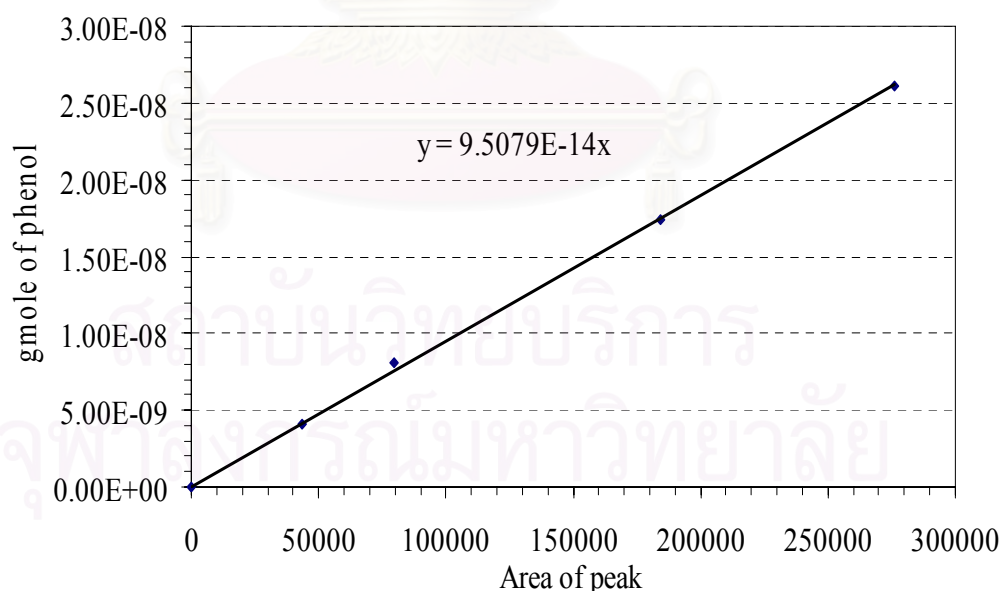
Figure C.1 The calibration curve of phenol.

APPENDIX D

CALCULATION OF BENZENE CONVERSION

The catalytic activity for the hydroxylation of benzene was evaluated in terms of benzene conversion and phenol productivity.

$$\text{benzene conversion (\%)} = 100 \times \frac{\text{Overall mole of phenol produce}}{\text{Initial mole of benzene}} \quad \text{(D1)}$$

$$\text{phenol product} = \text{Overall mole of phenol produce} \quad \text{(D2)}$$

where mole of phenol can be measured employing the calibration curve of phenol in Figure C.1, Appendix C.,i.e.,

$$\text{mole of phenol} = ((\text{area of phenol peak from integrator plot on GC-9A}) \quad \text{(D2)}$$
$$\times 9.5079 \times 10^{-14})$$

APPENDIX E

DATA OF EXPERIMENTS

Table E1 Data of Figure 5.25

Sample	Benzene conversion (%)
TS-1	0.188
Co-TS-1	9.851
V-TS-1	5.451
Fe-TS-1	3.314
Al-TS-1	2.028

Table E2 Data of Figure 5.26

Sample	Benzene conversion (%)	
	No pretreatment	With pretreatment
TS-1	0.188	1.130
Co-TS-1	9.851	14.775
V-TS-1	5.451	10.490
Fe-TS-1	3.314	7.040
Al-TS-1	2.028	3.954

Table E3 Data of Figures 5.27 and 5.28

Sample	Temperature(^{o}C)	Phenol productivity (mmole/g *s)	
		No pretreatment	With pretreatment
TS-1	50	1.173×10^{-7}	2.2×10^{-5}
	60	1.986×10^{-7}	5.3×10^{-5}
	70	5.028×10^{-7}	1.2×10^{-5}
	80	2.138×10^{-7}	1.6×10^{-5}
Co-TS-1	50	6.065×10^{-3}	8.189×10^{-3}
	60	6.589×10^{-3}	9.706×10^{-3}
	70	1.059×10^{-2}	1.587×10^{-2}
	80	1.15×10^{-3}	3.984×10^{-3}
V-TS-1	50	2.194×10^{-3}	6.494×10^{-3}
	60	3.913×10^{-3}	8.633×10^{-3}
	70	5.856×10^{-3}	1.169×10^{-2}
	80	1.306×10^{-3}	2.914×10^{-3}
Fe-TS-1	50	1.51×10^{-3}	2.202×10^{-3}
	60	1.74×10^{-3}	5.2×10^{-3}
	70	3.56×10^{-3}	7.567×10^{-2}
	80	7.7×10^{-4}	1.514×10^{-3}
Al-TS-1	50	5.6×10^{-3}	1.773×10^{-3}
	60	2.237×10^{-3}	2.175×10^{-3}
	70	1.059×10^{-2}	4.248×10^{-2}
	80	3.1×10^{-5}	9.35×10^{-3}

Table E4 Data of Figures 5.29 and 5.30

Sample	benzene/H_2O_2 molar ratio	Phenol productivity (mmole/g *s)	
		No pretreatment	With pretreatment
TS-1	0.5	8.605×10^{-8}	2×10^{-6}
	1	5.028×10^{-7}	1.217×10^{-3}
	1.5	6.278×10^{-7}	1.86×10^{-3}
	2	1.044×10^{-7}	2.72×10^{-3}
Co-TS-1	0.5	3.437×10^{-3}	1.462×10^{-3}
	1	1.058×10^{-2}	5.687×10^{-2}
	1.5	1.741×10^{-2}	8.928×10^{-2}
	2	2.357×10^{-2}	0.1245
V-TS-1	0.5	1.690×10^{-3}	1.359×10^{-2}
	1	5.898×10^{-3}	5.281×10^{-2}
	1.5	9.755×10^{-2}	7.377×10^{-2}
	2	1.574×10^{-2}	0.1064
Fe-TS-1	0.5	1.028×10^{-3}	3.367×10^{-3}
	1	3.43×10^{-3}	1.317×10^{-2}
	1.5	5.40×10^{-3}	2.469×10^{-2}
	2	8.44×10^{-3}	3.616×10^{-2}
Al-TS-1	0.5	8.17×10^{-5}	9.24×10^{-3}
	1	2.12×10^{-5}	6.268×10^{-3}
	1.5	3.68×10^{-5}	1.020×10^{-2}
	2	5.36×10^{-4}	1.614×10^{-3}

Table E5 Data of Figures 5.31 and 5.32

Sample	Time (hr)	Phenol productivity (mmole/g *s)	
		No pretreatment	With pretreatment
Co-TS-1	0.25	0.0253	0.1001
	0.5	0.0224	0.0935
	0.75	0.0198	0.0828
	1.00	0.0181	0.0810
	2.00	0.0128	0.0652
	3.00	0.0106	0.0569
	4.00	0.0080	0.0511
V-TS-1	0.25	0.0175	0.0879
	0.5	0.0133	0.0754
	0.75	0.0123	0.0717
	1.00	0.0109	0.0650
	2.00	0.0069	0.0477
	3.00	0.0059	0.0451
	4.00	0.0045	0.0403
Al-TS-1	0.25	0	1.2598×10^{-2}
	0.5	0	1.0716×10^{-2}
	0.75	1.2376×10^{-6}	9.1356×10^{-3}
	1.00	1.3976×10^{-6}	1.0293×10^{-2}
	2.00	7.5444×10^{-7}	8.1569×10^{-3}
	3.00	5.0275×10^{-7}	6.2683×10^{-3}
	4.00	3.9082×10^{-7}	5.1268×10^{-3}

Table E6 Data of Figures 5.31 and 5.32(continue)

Sample	Time (hr)	Phenol productivity (mmole/g *s)	
		No pretreatment	With pretreatment
Fe-TS-1	0.25	3.3369×10^{-3}	3.7260×10^{-2}
	0.5	3.0006×10^{-3}	2.5148×10^{-2}
	0.75	2.6303×10^{-3}	2.0776×10^{-2}
	1.00	2.6972×10^{-3}	2.2016×10^{-2}
	2.00	2.3981×10^{-3}	1.7460×10^{-2}
	3.00	2.1188×10^{-3}	1.3168×10^{-2}
	4.00	1.6215×10^{-3}	9.8981×10^{-3}

Table E7 Data of Figure 5.33

Sample	Volume of $KMnO_4$
TS-1	35
Co-TS-1	26
V-TS-1	21.5
Fe-TS-1	12
Al-TS-1	8.1

Table E8 Data of Figure 5.35

Sample	Time(hr)	%Adsorption of phenol
TS-1	0	0
	3	63
	11	72
Co-TS-1	0	0
	3	10
	11	18
V-TS-1	0	0
	3	32
	11	42
Fe-TS-1	0	0
	3	36
	11	47
Al-TS-1	0	0
	3	61
	11	68

APPENDIX F

MATERIAL SAFETY DATA SHEET OF
BENZENE AND HYDROGENPEROXIDE

Benzene

Safety data for benzene

General

Synonyms: benzol, phenyl hydride, coal naphtha

Molecular formula: C_6H_6

Physical data

Appearance: colourless liquid

Melting point: 5.5 °C

Boiling point: 80 °C

Specific gravity: 0.87

Vapour pressure: 74.6 mm Hg at 20 °C

Flash point: -11 °C

Explosion limits: 1.3 % - 8 %

Autoignition temperature: 561 °C

Stability

Stable. Substances to be avoided include strong oxidizing agents, sulphuric acid, nitric acid. Highly flammable.

Toxicology

This material is a known carcinogen. The risks of using it in the laboratory must be fully assessed before work begins. TLV 10 ppm. Short-term exposure may cause a variety of effects, including nausea, vomiting, dizziness, narcosis, reduction in blood pressure, CNS depression. Skin contact may lead to dermatitis. Long-term exposure may lead to irreversible effects. Severe eye irritant. Skin and respiratory irritant.

Personal protection

Safety glasses, gloves, good ventilation. Thought should be given to using an alternative, safer product.

Hydrogen Peroxide, 30% solution

Safety data for hydrogen peroxide, 30% solution

General

Synonyms: albone 30, albone 35, albone 50, albone 70, albone 35cg, albone 50cg, albone 70cg, interox, kastone, perone 30, perone 35, perone 50. Data also applies to solutions of similar strength.

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

Physical data

      Appearance: colourless liquid

      Melting point: ca. -28 °C

      Boiling point: ca. 114 °C

      Specific gravity: typically near 1.19

      Vapour pressure: 23.3 at 30 °C

Stability

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

Toxicology

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

Personal protection

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

APPENDIX G

LIST OF PUBLICATION

Kriangkrai Shenchunthichai and Tharathorn Mongkhonsi, "Catalytic study of Iron, Aluminium, Cobalt and Vanadium modified titanium silicalite-1 in the hydroxylation of benzene by hydrogen peroxide", 7th Nation Graduate Research Conference, Surat Thani, Thailand, April, 2007, Ref. No.O-21-Phys.

Kriangkrai Shenchunthichai, Darunee Sookhom and Tharathorn Mongkhonsi, "Preparation of Cu-TS-1", Proceedings of Thai Institute of Chemical Engineering and Applied Chemical Conference 16th, Bangkok, Thailand, Oct, 2006, Ref. No.CRE-007.

VITA

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