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ในเครื่องปฏิกรณ์แบบฟองแก๊ส



นางสาวปาดัสม์ มานิตย์

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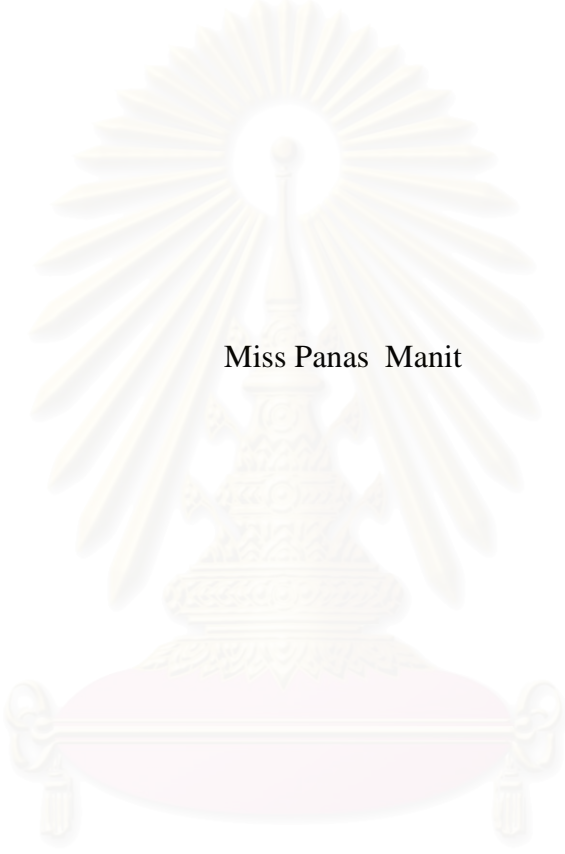
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HYDROXYLATION OF BENZENE TO PHENOL USING HYDROGEN  
PEROXIDE IN A BUBBLE REACTOR.



Miss Panas Manit

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

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                    **HYDROXYLATION OF BENZENE TO PHENOL  
USING HYDROGEN PEROXIDE IN A BUBBLE  
REACTOR.**


By                                 **Miss Panas Manit**

Field of Study                 **Chemical Engineering**


Thesis Advisor                **Associate Professor Tharathon Mongkhonsi, Ph.D.**

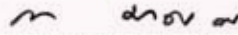
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Accepted by the Faculty of Engineering, Chulalongkorn University in Partial  
Fulfillment of the Requirements for the Master's Degree


  
.....Dean of the Faculty of Engineering  
(Professor Direk Lavansiri, Ph.D.)

THESIS COMMITTEE

  
..... Chairman  
(Associate Professor ML.Supakanok Thongyai, Ph.D.)

  
..... Thesis Advisor  
(Associate Professor Tharathon Mongkhonsi, Ph.D.)

  
..... Member  
(Amornchai Arpornwichanop, D.Eng.)

  
..... Member  
(Soipatta Soisuwan, D.Eng.)

ปาณัศม์ มานิตย์: ปฏิกริยาไฮดรอกซิเลชันของเบนซีนเป็นฟีนอลโดยใช้ไฮโดรเจนเปอร์ออกไซด์ในเครื่องปฏิกรณ์แบบฟองแก๊ส (HYDROXYLATION OF BENZENE TO PHENOL USING HYDROGEN PEROXIDE IN A BUBBLE REACTOR.)  
 อ. ที่ปรึกษา : รศ.ดร.ธราธร มงคลศรี, 73 หน้า

งานวิจัยนี้ได้ศึกษาการสังเคราะห์ฟีนอล โดยใช้ตัวเร่งปฏิกริยาไทเทเนียมซัลฟาโตด-1 ที่ผ่านการเพิ่มสมรรถนะด้วยสารละลายกรดไนตริก ในปฏิกริยาการไฮดรอกซิเลชันเบนซีน ด้วยไฮโดรเจนเปอร์ออกไซด์ ในเครื่องปฏิกรณ์แบบฟองแก๊ส ที่มีเบนซีนอยู่ในวัฏภาคแก๊ส ไฮโดรเจนเปอร์ออกไซด์อยู่ในวัฏภาคของเหลว และตัวเร่งปฏิกริยาที่แขวนในไฮโดรเจนเปอร์ออกไซด์อยู่ในวัฏภาคของแข็ง โดยศึกษาการปรับเปลี่ยนตัวแปรต่างๆ ของปฏิกริยา คือ อัตราการป้อนแบบเป็นจังหวะของเบนซีน ระยะเวลาในการทำปฏิกริยา และปริมาณตัวเร่งปฏิกริยาที่ใช้ในการทำปฏิกริยา ผลการศึกษาแสดงให้เห็นว่าการป้อนเบนซีนครั้งละน้อยๆ แต่มีความถี่ในการป้อนสูง ให้ค่าการเปลี่ยนของเบนซีนสูงกว่าการป้อนปริมาณเบนซีนครั้งละมากๆ แต่มีความถี่ในการป้อนต่ำ ทำให้เห็นว่าทั้งปริมาณการป้อนเบนซีนต่อครั้ง และความถี่ในการป้อนมีผลต่อค่าการเปลี่ยนของเบนซีน ดังนั้นจึงได้ทำการศึกษาเพิ่มเติมในส่วนของ การปรับเปลี่ยนปริมาณเบนซีนที่ทำการป้อน โดยให้ ความถี่ในการป้อนคงที่ พบว่าการป้อนเบนซีนปริมาณน้อยๆ ต่อครั้ง ให้ค่าการเปลี่ยนของเบนซีน คิดว่าการป้อนปริมาณเบนซีนมากๆ ต่อครั้ง และศึกษาการปรับเปลี่ยนความถี่ในการป้อน โดยให้ ปริมาณเบนซีนในการป้อนแต่ละครั้งคงที่ พบว่าการป้อนเบนซีนที่มีความถี่มากเกินไป ไม่ได้ส่งผล ให้ค่าการเปลี่ยนของเบนซีนสูงตาม ดังนั้นความถี่ในการป้อนเบนซีนต้องเหมาะสมกับ ความสามารถในการเกิดปฏิกริยา จึงจะสามารถทำให้ค่าการเปลี่ยนของเบนซีนดีขึ้น ในส่วน การศึกษาการเปลี่ยนแปลงระยะเวลาที่ใช้ในการเกิดปฏิกริยา พบว่าช่วงแรกของการเพิ่มระยะเวลา การเกิดฟีนอลจะมีค่าเพิ่มขึ้นเรื่อยๆ แต่เมื่อเพิ่มระยะเวลาให้มากขึ้นกว่าในช่วงแรก พบว่าการเกิดฟีนอล มีแนวโน้มคงที่ ไม่เพิ่มมากไปกว่าช่วงแรกอีก และการเพิ่มปริมาณตัวเร่งปฏิกริยาสามารถทำให้ ปฏิกริยาการไฮดรอกซิเลชันของเบนซีนเป็นฟีนอลเกิดได้ดีขึ้น ส่งผลให้ค่าการเปลี่ยนของเบนซีน เพิ่มขึ้น

จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา.....วิศวกรรมเคมี..... ลายมือชื่อนิสิต..... ภาณุวัฒน์ มานิตย์.....  
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##4870379221: MAJOR CHEMICAL ENGINEERING

KEY WORD: TITANIUM SILICALITE-1/ BENZENE/ PHENOL/ BUBBLE REACTOR / BENZENE PULSE INJECTION/ REACTION TIME/ THE AMOUNT OF CATALYST

PANAS MANIT: HYDROXYLATION OF BENZENE TO PHENOL USING HYDROGEN PEROXIDE IN A BUBBLE REACTOR. THESIS ADVISOR: ASSOC.PROF. THARATHON MONGKHONSI, Ph.D. 73 pp.

This research investigated the synthesis of phenol by hydroxylation of benzene using hydrogen peroxide over titanium silicalite-1 catalyst, that was pretreated with nitric acid, in a bubble reactor. In the reactor, benzene was fed in gas phase, hydrogen peroxide was liquid phase, and catalyst, which was immersed in hydrogen peroxide, was solid. The effect of key parameters such as rate of pulse feeding of benzene, reaction time and amount of catalyst were studied experimentally to demonstrate the cause-effect relationships in a bubble reactor. The comparison showed that at a fix amount of benzene to the fed, injecting a small amount of benzene in each pulse at high frequency yielded higher benzene conversion than injecting a large amount of benzene in each pulse at low frequency. In addition, the experiment at a fixed frequency of injection showed that injecting a smaller amount of benzene in each injection yielded a higher benzene conversion than injecting a larger amount of benzene in each injection. Moreover, the expandable experiment at a varied frequency of injection by fixing the amount of benzene feeding founded that the excess frequency of benzene feeding does not cause the increased benzene conversion. Hence, the frequency of benzene feeding had to suitable for the ability of phenol production in order to convert the high activity of benzene conversion. The study of reaction time showed that, in the initial section of increasing time, the produced phenol increased continuously. However, after initial section, the increasing of reaction time does not play a role on the produced phenol and the trend of the phenol is stable. The higher amount of catalyst in the hydroxylation of benzene to phenol enhanced the best benzene conversion.

Department.....Chemical Engineering... Student's signature.....*Panas Manit.*.....  
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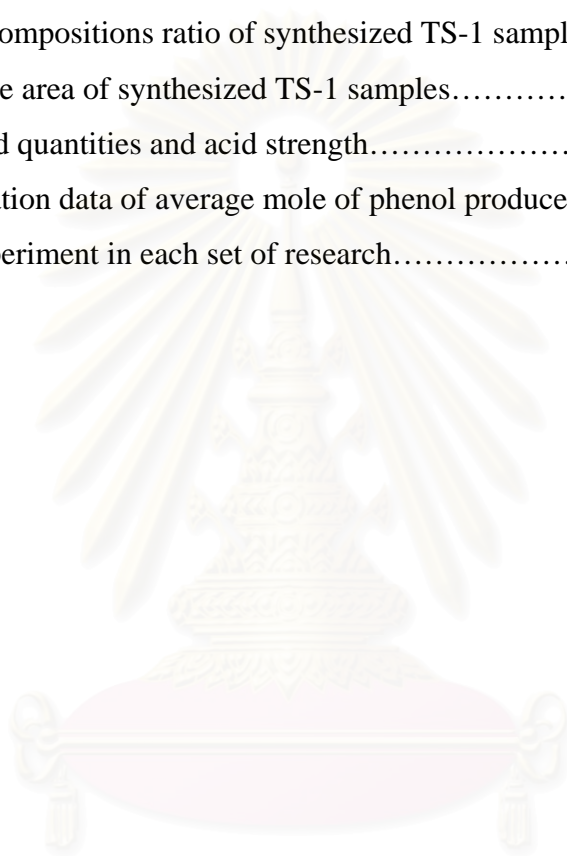
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## CHAPTER I

### INTRODUCTION

The German chemist, Runge, isolated phenol from coal tar in 1834, and he gave it the name *karbolsäure* (coal-oil acid or carboic acid), though its composition was not known until 1841. The name carboic acid can be misleading, as it does not contain the functional group normally associated with organic acids, even though it is slightly acidic.

Phenol has been in production since the 1860s. One of the early uses for phenol was as an antiseptic. Towards the end of the 19th century, industrial scientists found new uses for phenol in the synthesis of dyes, aspirin, and one of the first high explosives, picric acid. As early as 1872, it was found that phenol could be condensed with aldehydes (for example methanal) to make resinous compounds, a process still in use today. Phenol is also used to make chemical intermediates for a wide range of other applications, ranging from plastics to pharmaceuticals and agricultural chemicals.

Phenol was first manufactured commercially by distillation from coal tar, but the energy required and quantities produced meant this method could not be sustained. Synthesis by the sulphonation of benzene was implemented by BASF in 1899 and continued until the 1960s. One of its main disadvantages is the poor atom economy of the reaction, a factor that has become increasingly important as the chemical industry seeks to develop more sustainable processes. The sulphonation route produced large quantities of waste, and used aggressive reagents, and so several other methods, mostly using benzene as the starting point, were developed, though these also used reagents like chlorine, sodium hydroxide and hydrogen gas and so are not in use. One alternative method that has been in use since 1961 makes phenol by oxidising methylbenzene (toluene). Its disadvantage is that it requires considerably more energy.

The main method used to manufacture phenol since the 1960s has been through the oxidation of 1-methylethylbenzene, commonly called cumene, which is



made from benzene. The cumene process is combined with the fact that it is a three-step process with a potentially explosive intermediate. This process is called “coproduct” or “two-for-one” process and, in general, provide excellent economics if the ratio and volume of the two products match market demand. For the most part, this has been the case for phenol and acetone (~6 t of acetone is produced for every 10 t of phenol). There is some concern, however, especially in certain local situations, that acetone will be in oversupply because of a disproportionately growing demand for phenol. This concern has initiated efforts to develop non-coproduct phenol processes.

A potential route is the hydroxylation of benzene by hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). The reaction is normally carried out in liquid phase using TS-1. This reaction has gained attention due to several advantages. For example, the reaction is a one-step reaction, the reaction can occur at a relative low temperature (i.e. 70-80°C), using  $\text{H}_2\text{O}_2$  offers low cost per oxygen atom and the absence of by-products, it is clean and low toxic reaction (water as a co-product) and heterogeneous catalytic system allows simple separation and recovery of the catalyst from the reaction mixture. The reaction, however, still has some drawbacks to be overcome. The major drawbacks are the phase separation between the two reactants and the very low yield of the product.

There were many researchers who studied the effect of operating condition. The most common way, the reaction was studied in a stirred slurry reactor without the presence of any solvent. Some researchers have tried to improve the yield of phenol by adding some solvents to produce a single phase system. The reaction was performed in stirred slurry reactors by using solvents such as acetonitrile, acetone and methanol. This technique, however, possessed a major drawback, the difficulty to separate the phenol product and the unreacted reactants from the solvent phase.

The homogeneous contacting methods pose mixing problems of the benzene-rich and hydrogen peroxide-rich phases and will be complicated by mass transfer from the liquid phase to the solid surface. Moreover, TS-1 catalyst has some properties as a polar catalyst. Therefore, the TS-1 only interacted with the polar

substances, hydrogen peroxide, but not interacted with the non-polar, benzene. In a previous work, Chaijarat (2003) investigated to compare the flow of the benzene and hydrogen peroxide into the reactor between homogeneous and heterogeneous flow. This research suggested that the heterogeneous flow was enhanced benzene conversion higher than the homogeneous flow. Another work, Kamonsawat (2005) found that the benzene conversions of TS-1 catalyst pretreated with HNO<sub>3</sub> solution are higher than that of the unpretreated catalyst.

Moreover, TS-1 has the morphology and average pore size nearly as 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. Therefore, the bubble reactor is chosen as a reactor. The bubble column reactor are widely used in the chemical industry where heterogeneous gas-liquid or gas-solid reactions take place, particularly, in which the liquid phase controls mass transfer processes due to the relative insolubility of gases (Lye and Stuckey, 2001). Important applications of bubble columns include oxidation, hydrogenation, ozonolysis, alkylation, column flotation, wastewater treatment, etc.

The bubble reactor is chosen as the test reactor in the present work, owing to its simplicity and the fact that this reaction has not been studied in this type of reactor before in the past. The pretreated catalyst is interested from the increment of the benzene conversion in this reaction. Moreover, this reaction presented several contacting alternatives and dealt that the previous contacting methods posses mixing problems of the phenol-rich and H<sub>2</sub>O<sub>2</sub>-rich phases and will be complicated by mass transfer from the liquid phase to the solid surface (Thangaraj *et al.*, 1990; Tendulkar *et al.*, 1998; Bhaumik *et al.*, 1998; Bengoa *et al.*, 1998; Kumar *et al.*, 1999)

The contacting alternative explored in this investigation employed batch operation with vaporized benzene fed into reactor which has the pretreated TS-1 catalyst suspended in H<sub>2</sub>O<sub>2</sub> liquid solution filled.

In this study, the main objectives of this research is to investigate the alternative route of the oxidation properties of the pretreated Titanium Silicalite-1 (TS-1) catalyst in the hydroxylation reaction of benzene by hydrogen peroxide in optimum parameters in a bubble reactor. The research has been scoped as follows:

- 1) Preparation of TS-1 catalysts by using the hydrothermal method.
- 2) Pretreatment of these catalysts with solution of 5M HNO<sub>3</sub>
- 3) Characterization of the synthesized TS-1 catalysts by using the following techniques.
  - Determination of bulk composition of Si/Ti by X-ray fluorescence (XRF).
  - Determination of specific area by N<sub>2</sub> 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 synthesized catalysts by NH<sub>3</sub>-TPD technique.
- 4) Catalytic reactions in three phase hydroxylation of benzene at 70°C and vary parameters of reaction in order to find an optimum condition.

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 hydroxylation of benzene reactions, TS-1 catalysts in the past and comments on previous works.

The theory of this research, studies about the hydroxylation of benzene reaction and its possible mechanism, the properties of TS-1 catalysts, three phase catalytic reaction and a bubble reactor are presented in chapter III.

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

The experimental results, including an expanded discussion, are described in chapter V.

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

Finally, the sample of calculation of catalyst preparation, external and internal diffusion limitations, 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.



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## CHAPTER II

### LITERATURE REVIEW

TS-1 catalyzed processes are advantageous from the environmental point of view as the oxidant is aqueous  $\text{H}_2\text{O}_2$ , which turns into water, and the reactions, operated in liquid phase under mild conditions, show very high selectivity reducing problems and cost of by-product treatment. TS-1 can catalyze a variety of useful oxidation reactions and the hydroxylation of benzene by  $\text{H}_2\text{O}_2$  to phenol in the presence of TS-1 is also well known. An attempt will also be made to summarise the present knowledge and understanding of various factors influencing the conversion of the hydroxylation of benzene reaction.

#### 2.1 Literature reviews

Kraushaar-Czarnetzki and Van Hooff (1989) reported that TS-1 could also be obtained from [Al]ZSM-5 by dealumination and subsequent treatment with titanium tetrachloride. The obtained TS-1 exhibited the same catalytic properties as hydrothermal synthesized TS-1 of high purity. Moreover, their experimental result showed that the selectivity of their catalyst was strongly affected by the presence of small amounts of non-framework titania.

Thangaraj *et al.* (1990) studied the hydroxylation of benzene with  $\text{H}_2\text{O}_2$  over various zeolites. They found that benzene remained unreacted over silicalite-1,  $\text{TiO}_2$  (both amorphous and crystalline), and also in the absence of catalysts. The selectivity for the conversion of  $\text{H}_2\text{O}_2$  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.

TS-1 samples of different particle size were synthesized and investigated by Van der Pol *et al.* (1992). Smaller particles were more active than larger particles. From calculation of the Weisz modulus they concluded that large zeolite particle were not fully utilized because of pore diffusion limitations. The product distribution was also influenced by particle size.

Martens *et al.* (1993) studied the hydroxylation of phenol with  $H_2O_2$  on EUROTS-1 catalyst. They reported that the calcinations conditions of EUROTS-1 was critical. An increase of calcinations temperature from 400 to 500°C resulted in a substantial increase in activity. Static calcinations generated less active catalysts, probably due to incomplete removal of template or its residues. The higher *ortho/para* ratio in the hydroxylated products observed on EUROTS-1 that was calcined under static conditions was used as an indication to show that the active sites in the interior of the crystals were partially blocked. In the presence of small amounts of solvent, a replacement of acetone by methanol resulted in an increase of the *p*-selectivity of EUROTS-1.

Weitkamp *et al.* (1997) investigated samples of TS-1 which had different mole ratio of Si/Ti. They observed that samples prepared according to two different synthesis procedures could differ significantly in their hydrophobic/hydrophilic surface properties. For Si/Ti ratio above ca. 40, value of hydrophobic/hydrophilic decreased linearly with increasing titanium content which had been attributed to the increased formation of polar Si-O-Ti bridges in the zeolite framework. For TS-1 samples with higher titanium content, value of hydrophobic/hydrophilic strongly depended on the method of preparation and was considerably influenced by the formation of additional titanium-containing species in extra-framework positions. From the results of the catalytic characterization in the hydroxylation of phenol they could conclude that, in particular, TS-1 samples with high titanium content were the more active, the lower their value of hydrophobic/hydrophilic.

Bengoa *et al.* (1998) studied the influence of TS-1 structural properties and operating conditions on benzene catalytic oxidation with  $\text{H}_2\text{O}_2$ . They mentioned that small changes in the preparation conditions led to the presence of extra-framework titanium. In the benzene hydroxylation reaction using TS-1 prepared by the method of Thangaraj *et al.* (1990), the presence of sodium traces in the solid or  $\text{CH}_3\text{OH}$  in the reaction mixture changed the activity drastically. These results were attributed to a deactivation of active  $\text{Ti}^{4+}$  sites. In addition, the synthesis conditions might be controlled carefully to get pure TS-1, since the presence of extra-framework titanium inhibited benzene hydroxylation.

Bhaumik *et al.* (1998) studied the influence of solvent conditions on benzene catalytic oxidation with  $\text{H}_2\text{O}_2$ . 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/ $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  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/ $\text{H}_2\text{O}_2$  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 biphasic 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 biphasic 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 biphasic while such a resistance was minimized in triphase.

Li *et al.* (2001) reviewed the effect of titanium species in TS-1 prepared by hydrothermal method on the catalytic activity. They reported that the form of titanium atoms incorporated into the framework of TS-1 synthesized using tetrapropylammonium bromide as template differed from that using the classical method. But the symmetry of TS-1 changed from monoclinic to orthorhombic with the increase of titanium content in both methods. The  $\text{Ti-O}_2^-$  originated from framework titanium and  $\text{H}_2\text{O}_2$  had the moderate stability and might be active site in oxidation reaction. TS-1 synthesized using tetrapropylammonium bromide as template did not contain anatase, but contained a kind of partly condensed titanium species with six-fold coordination. The titanium species might correspond to 270-280 nm band in UV-VIS spectra and also could form  $\text{Ti-O}_2^-$ . But, this kind of  $\text{Ti-O}_2^-$  was very stable and could not be catalytic active site. Therefore, the six-fold coordination titanium species might be inactive in both the oxidation reaction and the decomposition of  $\text{H}_2\text{O}_2$ . The hypothesis had been further proved by the phenomena that the titanium species was easily washed off using acid, and acid treating would not influence the catalytic performance of TS-1.

Liu *et al.* (2004) studied the influence of pretreatment with aqueous solution of  $\text{CH}_3\text{COOK}$ ,  $\text{NaAc}$ ,  $\text{NH}_4\text{Ac}$ ,  $\text{NH}_4\text{Cl}$ , or  $\text{HNO}_3$ . 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  $\text{TiO}_2$  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  $\text{H}_2\text{O}_2$  and the hydroquinone/chatacol 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.

Kong *et al.* (2004) studied the selective oxidation of thiophene by hydrogen peroxide with different SiO<sub>2</sub>/TiO<sub>2</sub> ratio of TS-1 catalyst. The catalyst was treated using HCl (2 mol/l) four times, part of the non-framework titanium species will be washed off and the activity of the catalyst increased greatly. These results indicate that framework titanium was crucial for thiophene oxidation. The unique role played by framework titanium might be that they could interrupt conjugation during the reaction. This breakage of the aromatic of thiophene ring was critical for oxidation of thiophene by hydrogen peroxide under mild conditions. Non-framework titanium in the catalyst was not the active site for thiophene oxidation.

Hulea and Dumitriu (2004) studied Ti-containing molecular sieves with MFI(TS-1), BEA(Ti-beta) and MCM-41 topologies for the styrene oxidation in liquid phase by hydrogen peroxide was performed. The major reactions were epoxidation of styrene oxide into phenylacetaldehyde as well as its oxidative cleavage into benzaldehyde and formaldehyde. A high selectivity to phenylacetaldehyde was observed over TS-1, whereas the benzaldehyde formation was predominant on Ti-beta and TiMCM-4. Because of the diffusion limitation of the reactants and shape-selectivity towards the transition state and the product distribution depended on the nature of the catalyst. Thus, the selectivity to phenylacetaldehyde was very high for all catalysts of MFI type (smaller pore opening), whereas the benzaldehyde was formed in large amount in the presence of Ti-beta and TiMCM-41 (larger pores).

Liu *et al.* (2005) studied deactivation and regeneration of TS-1/diatomite catalyst for hydroxylation of phenol in a fixed-bed reactor. They found that the TS-1/diatomite catalyst would be deactivated during the hydroxylation of phenol by H<sub>2</sub>O<sub>2</sub> in the fixed-bed reactor, and the catalytic activity and selectivity to products decrease with an increase of reaction time. However, the crystallinities of the TS-1/diatomite catalyst had changed a little, and the framework structure of TS-1/diatomite catalyst had changed a little, and the framework structure of TS-1 zeolite and the amount of titanium in the framework had not changed. Compared with the fresh catalyst, the

BET surface area and pore volume of the deactivated catalyst decreased significantly, and the channels of the TS-1/diatomite catalyst were blocked by the organic by-products deposited on the catalyst surface, resulting in the reversible deactivation of the catalyst. The deposition on the TS-1/diatomite catalyst could be removed by calcining at 550°C in air or refluxing with dilute hydrogen peroxide, which could recover completely the performance of the TS-1/diatomite catalyst for phenol hydroxylation.

Moreover, Liu et al. (2005) studied a synthesis of TS-1 using amorphous SiO<sub>2</sub> and its catalytic properties for hydroxylation of phenol in fixed-bed reactor. Titanium silicalite-1 (TS-1) has been synthesized using amorphous SiO<sub>2</sub> as silicon source and tetrapropylammonium bromide (TPABr) as template. They found that the synthesis conditions have a great influence on the physicochemical and catalytic properties of TS-1. The crystallinity of the sample increases with increasing crystallization temperature, crystallization time, SiO<sub>2</sub>/TiO<sub>2</sub>, SiO<sub>2</sub>/H<sub>2</sub>O or n-butylamine (NBA)/SiO<sub>2</sub>. An increase of the aging time, H<sub>2</sub>O/SiO<sub>2</sub>, SiO<sub>2</sub>/TiO<sub>2</sub> or NBA/SiO<sub>2</sub> is in favor of gaining the sample with smaller crystal size. On the contrary, increasing the crystallization temperature and time, or TPABr/SiO<sub>2</sub> can increase the crystal size of sample. The amount of Ti<sup>4+</sup> incorporated into framework of TS-1 zeolite is affected hardly by the crystallization temperature, aging time, H<sub>2</sub>O/SiO<sub>2</sub> or TPABr/SiO<sub>2</sub>. However, the high ratio of NBA/SiO<sub>2</sub> or TiO<sub>2</sub>/SiO<sub>2</sub> in the matrix gel promotes Ti incorporating into the framework of TS-1. Adding nonionic surfactant as an additive in the synthesis gel, can increase the amount of framework Ti, and reduce the crystal size of sample and the amount of TiO<sub>2</sub> outside framework. Smaller crystal size and more amount of framework Ti are favorable to increase the catalytic performance of TS-1 for the hydroxylation of phenol with H<sub>2</sub>O<sub>2</sub> in the fixed-bed reactor system.

In 2006, Liu et al. studied the chemical kinetics of hydroxylation of phenol with 30% H<sub>2</sub>O<sub>2</sub> over the TS-1/diatomite catalyst in a fixed-bed reactor system at 50-90°C. The factors affecting the hydroxylation of phenol catalyzed by the TS-1/diatomite catalyst in the fixed-bed reactor system, as well as their kinetic characteristics are obtained. The rate of hydroxylation of phenol increases with the increase of reaction temperature, phenol concentration and H<sub>2</sub>O<sub>2</sub> concentration. The rate of hydroxylation of phenol is near first order toward the concentration of phenol,

and zero to first order toward the concentration of  $\text{H}_2\text{O}_2$ . Meanwhile, the rate of  $\text{H}_2\text{O}_2$  decomposition increases also with the increase of reaction temperature and  $\text{H}_2\text{O}_2$  concentration.

Molinari et al. (2006) investigated one-step production of phenol by selective oxidation of benzene with hydrogen peroxide in biphasic system. The reaction was carried out in a biphasic system separated by a catalytic membrane reactor. This new system showed a high selectivity to phenol, minimizing its over-oxidation in over-oxygenated by-products. The effect of various reaction parameters such as the addition of hydrogen peroxide mode, amount of hydrogen peroxide, type of membrane, type of catalyst and organic acid was investigated. The report shows that iron(II)sulphate as catalyst, 18 mmol of hydrogen peroxide pumped for 4 h in the bulk of the aqueous phase as oxidant, acetic acid and polypropylene hydrophobic porous support as separation barrier, gave the best system performance in terms of phenol productivity ( $38.20 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ), selectivity to phenol (99.94%), benzene conversion to phenol (1.20%), and hydrogen peroxide conversion to phenol (96.78%).

## 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  $\text{H}_2\text{O}_2$  over the TS-1. However there are only some researches about the hydroxylation of benzene by  $\text{H}_2\text{O}_2$  although this is a simple reaction (it yields only two products). From the reviewed literatures, the TS-1 catalyst, which was synthesized by hydrothermal method, had high purity (Kraushaar-Czarnetzki and Van Hooff, 1989). The high purity of the TS-1 catalyst was required because the presence of extra-framework titanium inhibited benzene hydroxylation (Bengoa et al., 1998). One of the methods that makes the TS-1 has a high purity is the pretreatment of the catalyst. Therefore, the pretreatment of the TS-1 catalyst has importance to increase the activity of the catalyst. The effect of pretreatment with acid solution makes them more activity than that unpretreatment (Liu et al., 2004). From Liu et al. (2004), it is indicate that the activity increases because  $\text{TiO}_2$  anatase is removed to surface the TS-1 catalyst. Moreover, the increasing of calcinations temperature to  $500^\circ\text{C}$  could be increased the activity of the TS-1 due to removal of the template or its residues (Martens et al., 1993). The

selectivity to phenol of the benzene hydroxylation with  $H_2O_2$  over the zeolite was increased when using the TS-1 as the catalyst (Thangaraj et al., 1990). The particle size of the TS-1 had the influence on catalytic activity. It resulted that large zeolite particle were not fully utilized because of pore diffusion limitation (Van der pol et al., 1992). Thus, the hydroxylation reaction might occur primarily on the external surface of catalyst particle. Moreover, Liu et al. (2005) reported that smaller crystal size and more amount of framework titanium are favorable to increase the catalytic performance of TS-1. In addition, Weitkamp et al. (1997) found that TS-1 samples with high titanium content were the more active. All of the results support that the TS-1 catalyst should have the high purity, small size, more amount of titanium in framework and disappearance of the titanium extra-framework.

There are many perseverance about the increasing of the benzene conversion. Bhaumik e al. (1998) found that a triphase system was higher the conversion than biphasic system. Moreover, Kumar et al. (1999) reported that the reaction rates of the hydroxylation were enhanced under triphase conditions compared to that obtained under biphasic conditions. However, Molinari et al. (2006) studied this reaction in a biphasic system separated by a catalytic membrane reactor, the selectivity to phenol is 99.94% and the benzene conversion to phenol is only 1.20%.

Although, many researches of the hydroxylation of benzene were investigated in triphase system, but the previous studies did not show research in the bubble reactor and the benzene conversion in the researches is rather low. Thus, the hydroxylation of benzene by  $H_2O_2$  using the pretreated TS-1 catalysts in the bubble reactor is chosen to be studied in this research.

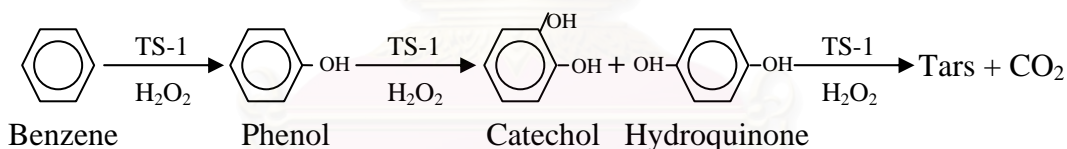


## CHAPTER III

### 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 (Figure 3.1). Acetone, methanol, 2-butanone or just water is suitable reaction media (Romano *et al.*, 1990; Khouw *et al.*, 1994; Thangaraj *et al.*, 1990). In aqueous solution, benzoquinone is also found, in appreciable amounts, among the products. Hydroxylation of benzene with a mixture of hydrogen and oxygen, an in situ source of hydrogen peroxide, can be achieved on Pd-containing TS-1 (Tatsumi *et al.*, 1992). This is, in principle, an easier route to phenol than that based on the preformed oxidant (Clerici and Ingallina, 1998). In practice, it proved less effective, because of faster catalyst decay.



**Figure 3.1** Direct hydroxylation of benzene over titaniumsilicalite-1 (TS-1) catalyst

#### 3.2 Titanium silicalite (Notari, 1989)

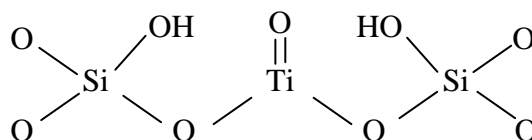
Titanium silicalite is an interesting material obtained by isomorphic substitution of trivalent metals or tetravalent metals in the framework of crystalline aluminosilicates or silicates. Titanium silicalites with MFI (TS-1) and MFI/MEL (TS-2) structures have been used in several oxidation reactions with  $\text{H}_2\text{O}_2$  as the oxidizing agent (Centi *et al.*, 2001).

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  $\text{Ti}^{\text{IV}}$  compounds

immediately shows that  $\text{Ti}^{\text{IV}}$  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  $\text{Ti}^{\text{IV}}$  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  $\text{Ti}^{\text{IV}}$ , tetrahedral coordination is also observed. Coordination of seven in a pentagonal pyramidal arrangement like in peroxo compounds and of eight like in  $\text{Ti}(\text{NO}_3)_4$  are also observed.

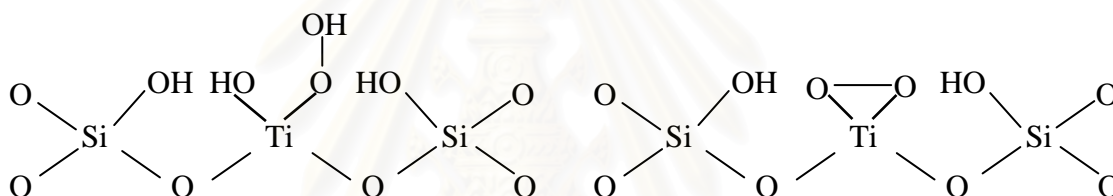
From the crystalline structure and the regular change in unit cell parameters which are consistent with isomorphous substitution of  $\text{Si}^{\text{IV}}$  with  $\text{Ti}^{\text{IV}}$  it seems justified to represent TS-1 as a silicalite in which few  $\text{Ti}^{\text{IV}}$  have taken the place of  $\text{Si}^{\text{IV}}$ . The interpretation of the catalytic activity of TS-1 must take into consideration the role played by these few  $\text{Ti}^{\text{IV}}$ : in fact pure silicalite is totally inactive, and other phases containing Ti have not been identified. Due to the fact that TS-1 crystallizes from a homogeneous solution, it is reasonable to assume that the distribution of  $\text{Ti}^{\text{IV}}$  in the crystal lattice is at random; since the Si/Ti ratio is in the range 40 - 90 in typical preparations, most  $\text{Ti}^{\text{IV}}$  must be isolated from each other by long sequences of -O-Si-O-Si-O-. If  $\text{Ti}^{\text{IV}}$  replaces a  $\text{Si}^{\text{IV}}$ , it should be tetrahedrally coordinated by  $\text{O}^-$ . However, the presence of a band at  $980\text{ cm}^{-1}$  closely corresponds to the band observed in other titanium compounds containing the  $\text{Ti}=\text{O}$  group, whose stretching frequency is  $975\text{ cm}^{-1}$  with bond distances of  $1.66 - 1.79\text{ \AA}$ ; 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  $\text{Ti}^{\text{IV}}$  are occupied by  $\text{Si}^{\text{IV}}$  which in a field of  $\text{O}^-$  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 is shown in figure 3.2



**Figure 3.2**  $\text{Ti}^{\text{IV}}=\text{O}$  group in TS-1 catalyst

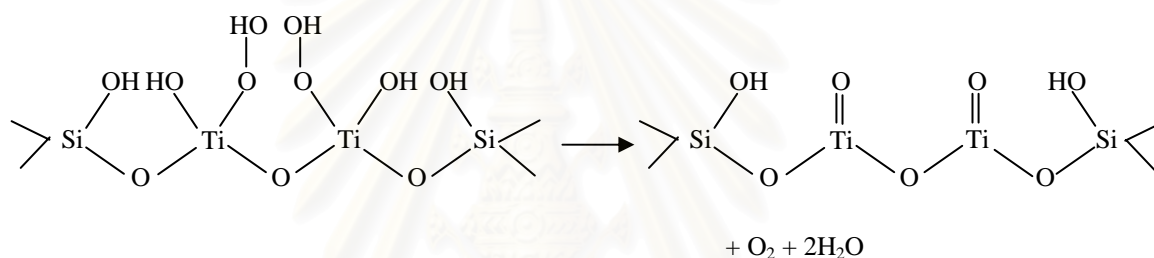
Other more elaborated and detailed representations could be given, should the present model prove inadequate to interpret all experimental facts.  $\text{Ti}^{\text{IV}}$  in TS-1 maintains the strong affinity of soluble  $\text{Ti}^{\text{IV}}$  salts for  $\text{H}_2\text{O}_2$  and in fact the addition of  $\text{H}_2\text{O}_2$  gives rise to a strong yellow colour which can be attributed to the formation of surface titaniumperoxocompounds which can be in the hydrated or dehydrated form and which constitutes the actual oxidants (Figure 3.3).



**Figure 3.3** Titaniumperoxocompounds on TS-1 catalyst surface

Work carried out on Mo(VI) and W(VI) peroxo compounds has demonstrated that peroxo compounds can act as oxidants in stoichiometric epoxidations involving a nucleophilic attack of the substrate to the peroxidic oxygen: in the presence of excess  $\text{H}_2\text{O}_2$  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  $\text{Ti}(\text{IV})$  peroxo compounds. The relevance of isolated  $\text{Ti}^{\text{IV}}$  and the connection with catalytic performances appears to hold also for the  $\text{TiO}_2/\text{SiO}_2$  catalyst. In fact high epoxide selectivities are obtained when  $\text{TiO}_2$  is distributed on high surface area  $\text{SiO}_2$  and its concentration is limited to 2%. It is very likely that at this low concentration  $\text{Ti}^{\text{IV}}$  are isolated and surrounded by  $\text{Si}^{\text{IV}}$ . Furthermore,  $\text{SiO}_2$  or  $\text{TiO}_2$  alone, or physical mixtures of  $\text{SiO}_2$  and  $\text{TiO}_2$  or various metal titanates exhibit no significant activity. Similarly, supporting  $\text{TiO}_2$  on carriers different from  $\text{SiO}_2$  like  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  or  $\text{ZrO}_2$  leads to catalysts whose activity is lower or nil. One piece of

evidence seems very convincing: when the  $\text{TiO}_2$  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  $\text{TiO}_2$  can have is an increase in the degree of dispersion of each  $\text{Ti}^{\text{IV}}$ : chances for each  $\text{Ti}^{\text{IV}}$  of having  $\text{Si}^{\text{IV}}$  as near neighbours increase, as does the selectivity of the catalyst. The correlation between the isolated  $\text{Ti}^{\text{IV}}$  and selectivity of the catalyst in epoxidation could be due to the fact that on  $\text{Ti}^{\text{IV}}$  having other  $\text{Ti}^{\text{IV}}$  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  $\text{H}_2\text{O}_2$  or hydroperoxides to  $\text{O}_2$  (Figure 3.4). This mechanism could not operate on perfectly isolated  $\text{Ti}^{\text{IV}}$ .



**Figure 3.4** Bimolecular interaction of surface peroxo species

Low decomposition of  $\text{H}_2\text{O}_2$  (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  $\text{TiO}_2/\text{SiO}_2$  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.

### 3.3 Three-phase Catalytic Reactions (Gas-Liquid-Solid)

In fine-chemical productions three-phase reaction systems are common for the hydrogenation and hydrogenolysis of different organic functional groups. Other reactions, such as heterogeneously catalyzed catalytic oxidations, hydrodesulfurizations, and reductive aminations are encountered less frequently.

The three phases present in this kind of reaction are a gas phase, containing, e.g., hydrogen or oxygen, a liquid phase, often consisting of a solvent, containing the dissolved reactants, and the solid catalyst. Besides dissolving the reactants, the solvent also provides a liquid layer around the catalyst particles, which might help to:

- avoid deactivating deposits and thus ensure higher catalyst effectiveness;
- achieve better temperature control because of the higher heat capacity of liquids; and
- modify the active catalyst sites to promote or inhibit certain reactions.

Besides these positive effects there is, however, a disadvantage—an extra barrier is introduced between the gaseous reactants (e.g., hydrogen) and the catalyst (see Figure 5). Mass transfer of the gaseous reactant to the liquid phase is often, but not always, the limiting step.

The organic substrate is usually present at much higher concentrations than the hydrogen dissolved in the liquid; hydrogen is the ‘limiting’ reactant. Therefore, the rate of mass transfer of hydrogen is of predominant significance. As shown in Figure 5, a number of steps must occur before hydrogen can be converted to products. The major steps are: (i) mass transfer from the gas bubble to the liquid, (ii) mass transfer from the liquid to the external surface of the catalyst particle, and (iii) diffusion inside the pores of the catalyst particle, accompanied by chemical reaction.

Mass transfer from the gas phase to the surface of the catalyst particle, i.e. external mass transfer, takes place by a number of steps in *series*. In contrast, diffusion inside the particle (internal mass transfer) and reaction occur *simultaneously*.

### **1. External mass transfer**

In the absence of internal diffusion limitations (i.e. diffusion inside the catalyst particle is much faster than reaction and  $c = c_s$ ), the observed rate of reaction thus equals:



$$r^{obs} = \kappa_1 a_1 (c_i - c_1) = \kappa_s a_s (c_1 - c_s) = \kappa c_g$$

and is determined by the slowest step.  $p = \text{H}_2$  pressure (bar);  $c = \text{H}_2$  concentration inside particle, dependent on distance from surface ( $\text{mol ml}_1^{-3}$ );  $c_i = \text{H}_2$  concentration at interface;  $c_1$  in bulk liquid,  $c_g$  at catalyst surface ( $\text{mol ml}_1^{-3}$ );  $r^{obs} =$  observed rate of reaction ( $\text{mol ml}_1^{-3} \text{ s}^{-1}$ );  $k_l =$  mass-transfer coefficient from liquid film to bulk liquid ( $\text{m}_r^3 \text{ m}_i^{-2} \text{ s}^{-1}$ );  $a_l =$  gas-liquid interfacial area per unit volume of reactor ( $\text{m}_i^{-2} \text{ m}_r^{-3}$ );  $k_s =$  mass-transfer coefficient from bulk liquid to catalyst surface ( $\text{m}_r^3 \text{ m}_i^{-2} \text{ s}^{-1}$ );  $a_s =$  liquid-solid interfacial area per unit volume of reactor ( $\text{m}_i^{-2} \text{ m}_r^{-3}$ );  $k =$  reaction rate constant for first-order reaction ( $\text{s}^{-1}$ ).

## 2. Internal Mass transfer

Inside the catalyst pellet diffusive occurs simultaneously with reaction. This leads to an internal concentration profile: at higher penetration depths the concentration of the reactants becomes lower due to partial conversion to reaction products. For positive reaction orders, this lower concentration results in a less efficient utilization of the catalyst particle, i.e. to so-called internal diffusion limitations. A measure for the degree of internal diffusion limitations is given by the effectiveness factor,  $\eta$ ,

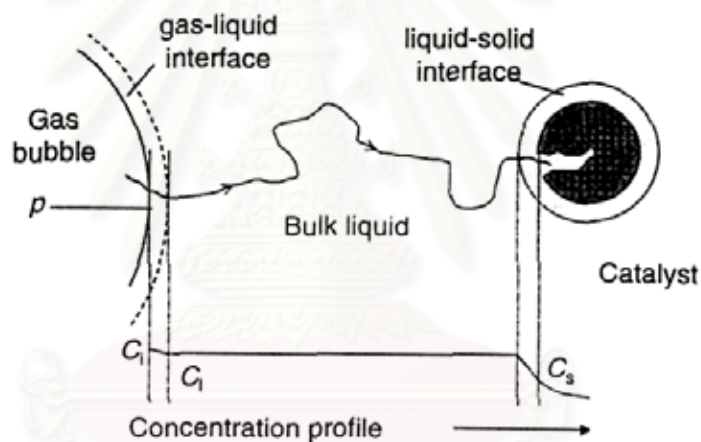
The simplest expression for the internal effectiveness factor results from irreversible first-order kinetics and a slab geometry for the pellet:

$$\eta = \frac{\tanh \phi}{\phi} \quad \text{and} \quad \phi = L \sqrt{\frac{\kappa}{D_{eff}}}$$

with  $\phi$  the Thiele modulus,  $L$  the length of the catalyst slab ( $\text{m}_p$ ), and  $D_{eff}$  the effective diffusion coefficient ( $\text{m}_p^2 \text{ s}^{-1}$ ).

Therefore, in the choice and design of three-phase reactors, not only must the intrinsic kinetics be considered, but also the mass-transfer characteristics. For

example, it is useless to try and improve the reaction rate by using a more active catalyst or increasing the catalyst load, when the overall rate of reaction is determined by mass transfer from the gas bubbles to the liquid phase, i.e. when the latter is slow compared with the intrinsic rate of reaction. Instead, one should try to increase the gas-to-liquid mass transfer rate, for example by improving mixing conditions. When the diffusion in the interior of the catalyst particles is rate determining, not only are the rates often reduced but selectivities are also affected. In this circumstance one should consider using smaller catalyst particles to improve liquid-to-solid mass transfer. Egg-shell catalysts, in which the active catalyst species is located in the outer shell of the catalyst particle, might also be used to improve selectivity (Figure 3.5).



**Figure 3.5** Mass transfer of hydrogen in gas/liquid/solid catalyst system; transport of  $H_2$  limiting;  $p = H_2$  pressure;  $C = H_2$  concentration,  $C_i$  at interface,  $C_l$  in bulk liquid,  $C_s$  at catalyst surface.

### 3.4 Bubble column reactor

Bubble column reactor is widely used for conducting gas-liquid reactions in a variety of practical applications in industry such as absorption, fermentations, bio-reactions, coal liquefaction and waste water treatment. Due to their simple construction, low operating cost, high energy efficiency and good mass and heat transfer, bubble columns offer many advantages when used as gas-liquid contactors.

In all these processes gas holdup,  $\varepsilon_g$ , and bubble size distribution are important design parameters, since they define the gas-liquid interfacial area available for mass transfer ( $\alpha$ ), which is given by:

$$\alpha = \frac{6\varepsilon_g}{d_{32}}$$

where  $d_{32}$  is the mean Sauter diameter of the bubble size distribution.

Depending on the gas flow rate, two main flow regimes are observed in bubble columns, i.e. the homogeneous bubbly flow regime and the heterogeneous regime. The homogeneous regime is encountered at relatively low gas velocities and characterized by a narrow bubble size distribution and radially uniform gas holdup and is most desirable for practical applications, because it offers a large contact area. Bubble size distribution and gas holdup in gas-liquid dispersions depend extensively on column geometry, operating conditions, physico-chemical properties of the two phases and type of gas sparger. The design of bubble columns has primarily been carried out by means of empirical or semi-empirical correlations based mainly on experimental data. The scale up of bubble columns is still poorly understood due to the complexity of flow patterns and their unknown behavior under different sets of design parameters such as diameter, height to diameter ratio, gas sparger type, physical properties of the liquid etc.

In bubble columns, agitation of the liquid phase and hence suspension of the catalyst is effected by the gas flow. Gas recycle causes more turbulence and thus better mixing. Often, circulation of the liquid is required to obtain a more uniform suspension. This can either be induced by the gas flow (airlift loop reactor) or by an external pump. In the latter case, it is possible to return the slurry to the reactor at high flow rate through an ejector (venturi tube). The local under-pressure causes the gas to be drawn into the passing stream, thus providing very efficient mixing. This type of reactor is called a jet-loop or venturi reactor. Jet-loop reactors tend to replace stirred tank reactors in the most recent fine chemical hydrogenations. The external heat exchanger on the liquid circulation loop enables high heat removal capacity,

which is a great advantage in highly exothermic reactions. A limitation on the use of jet-loop reactors is that the catalyst must be compatible with the pump, i.e. possess low hardness and high attrition resistance.



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## CHAPTER IV

### EXPERIMENTAL

This chapter consists of experimental systems and procedures used in this study. The chapter is divided into three sections, i.e., catalyst preparation, catalyst characterization and reaction study in hydroxylation of benzene. The chemicals, apparatus and procedures for catalyst preparation are explained in section 4.1. The composition, structure and surface properties of the catalyst characterized by various techniques such as XRF, BET, XRD, IR, NH<sub>3</sub>-TPD and FT-IR 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

The details of chemicals used in the preparation procedure of TS-1 are shown in Table 4.1.

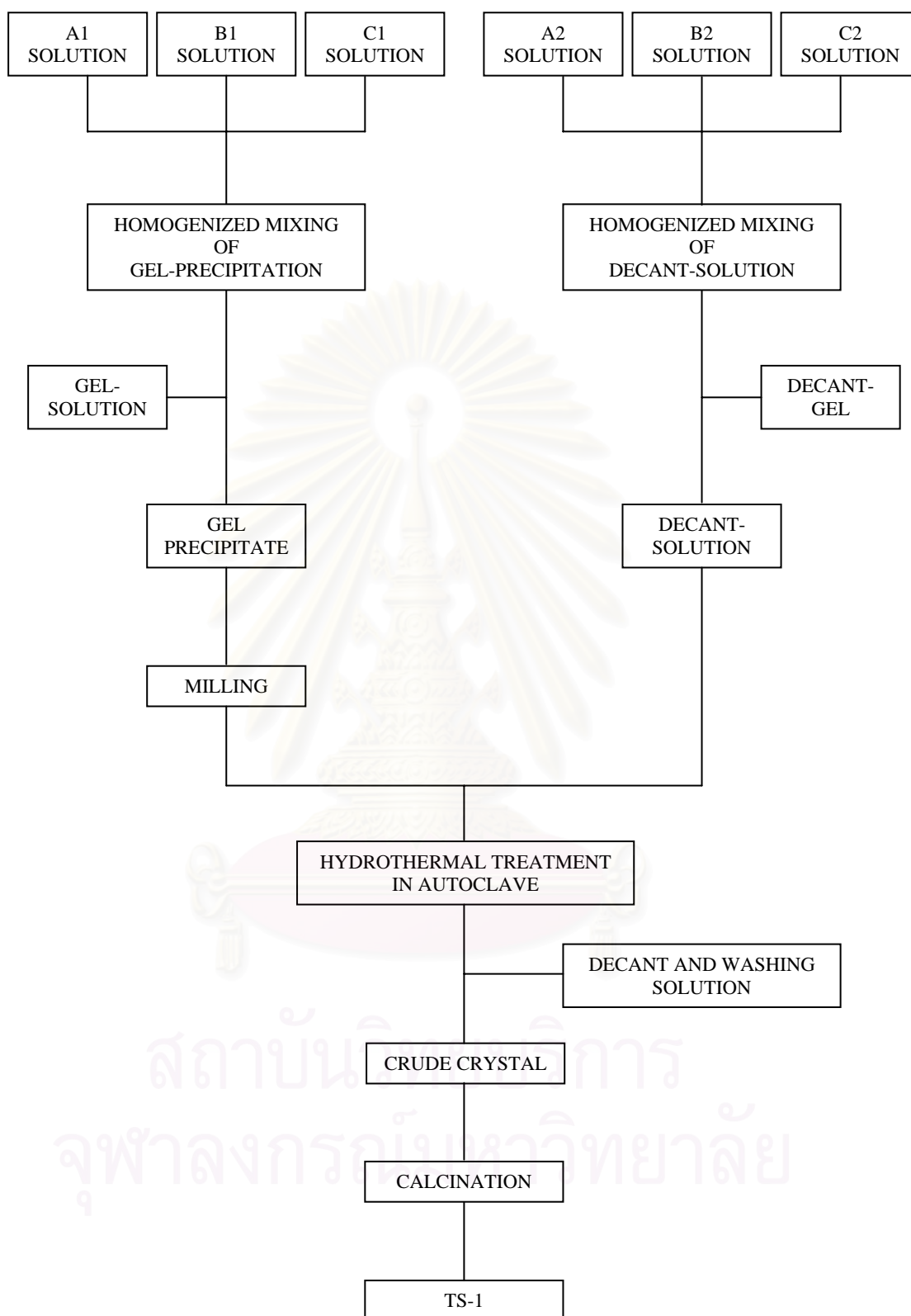
**Table 4.1** The chemicals used in the catalyst preparation

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

##### 4.1.2 Preparation Procedures

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





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

**Table 4.2** Reagents used for the preparation of TS-1

Solution for the gel preparation			Solution for decant-solution preparation		
Solution A1			Solution A2		
Ti[O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> ] <sub>4</sub>	2.87	g	Ti[O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> ] <sub>4</sub>	2.87	g
TPABr	5.72	g	TPABr	7.53	g
NaCl	11.95	g	De-ionized water	60.00	ml
De-ionized water	60.00	ml	H <sub>2</sub> SO <sub>4</sub> (conc.)	3.40	ml
H <sub>2</sub> SO <sub>4</sub> (conc.)	3.40	ml			
Solution B1			Solution B2		
Sodium silicate	69.00	g	Sodium silicate	69.00	g
De-ionized water	45.00	ml	De-ionized water	45.00	ml
Solution C1			Solution C2		
TPABr	2.16	g	NaCl	26.27	g
NaCl	40.59	g	De-ionized water	104.00	ml
NaOH	2.39	g			
De-ionized water	208.00	ml			
H <sub>2</sub> SO <sub>4</sub> (conc.)	1.55	ml			

#### 4.1.2.1 Preparation of Gel Precipitation and Decantation Solution

A supernatant liquid was separated from the gel, which is important for preparing the uniform crystals. 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<sub>2</sub>SO<sub>4</sub> (conc.) or NaOH solution were used to adjust pH of 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 1 h by a powder miller 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.

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 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<sup>2</sup> gauge. The mixture 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 crystal products were washed with de-ionized water until pH 7 by centrifugation in order to remove Cl<sup>-</sup> from the crystals. Then the crystals were dried in an oven at 110°C for 24 h.

#### **4.1.2.3 Calcination**

The dry crystals were calcined in an static air at 540°C and held at that temperature for 7 h, by heating them from room temperature to 540°C using a heating rate 10°C/min, to burn off the organic template and leave the cavities and channels in the crystals. The calcined crystals were finally cooled down to room temperature.

#### **4.1.3 Pretreatment catalysts**

TS-1 was placed into a round bottom flask and then 5M of 70% HNO<sub>3</sub> aqueous solution (Analytical Grade, APS) was added. After reflux at 80°C for 3 h, the pretreated catalyst was filtered, washed with distilled water until all remaining acid was washed out, dried at 110°C and calcined at 540°C for 7 h in static air.

## 4.2 Catalyst characterization

### 4.2.1 Determination of composition content of catalysts

The composition analysis of elements in the bulk of the catalyst was performed by X-ray fluorescence (XRF) using ED-XRF model ED-2000 at Scientific and Technological Research Equipment Centre, Chulalongkorn University.

### 4.2.2 BET surface area measurement

A sample cell which contained 0.3 g of sample was placed into BET Micromeritics 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, using Cu K $\alpha$  radiation with Ni filter. The operating conditions of measurement are shown below :

2 $\theta$ range of detection	:	6-40 $^{\circ}$
Resolution	:	0.02 $^{\circ}$
Number of scan	:	15

### 4.2.4 Fourier transform Infrared (FT-IR)

The functional group on the catalyst surface was determined by FT-IR using Nicolet model Impact 6700 with SMART DIFFUSE REFLECTANCE. Infrared spectra were recorded between 400 and 1200 cm $^{-1}$  on a microcomputer.

## 4.2.5 Ammonia Temperature Program Detector (NH<sub>3</sub>-TPD)

### 4.2.5.1 Measuring procedure

A sample cell which contained 0.1 g of sample was placed into Micromeritics Chemisorb 2750. Helium gas with flow rate at 15 ml/min was released to flow through the sample. The sample was heated from room temperature to 540°C with heating rate of 10°C/min and held at this temperature for 1 h. The sample was cooled down to 80°C and ready to measure the surface area. There were three steps to measure the surface area.

#### 1) Adsorption step

The 15 vol% ammonium gas with flow rate at 15 ml/min was flowed through the sample instead of helium, and held for 15 minutes.

#### 2) Desorption step

##### 2.1) Physi-sorption

The helium gas at the same flow rate was flowed through the sample instead of ammonium and also hold for another hour.

##### 2.2) Chemi-sorption

The sample was heated from 80°C to 540°C with a heating rate of 10°C/min. The signal from this step was recorded every 1 second and reported on a microcomputer.



### 4.3 Reaction study in hydroxylation of benzene

#### 4.3.1 Chemicals

The reactants used for the reaction study are shown in Table 4.3.

**Table 4.3** The chemicals used for the reaction study.

Chemical	Grade	Supplier
Benzene	Analytical	PS
Hydrogen peroxide 30%	Analytical	Merck
Ethanol	Analytical	Merck

#### 4.3.2 Apparatus

The catalytic test was performed in a flow system shown diagrammatically in Figure 4.2. 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:

##### 4.3.2.1 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 benzene flow through the bottom of the reactor.

##### 4.3.2.2 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 a sand bath which heated temperature at 130°C and used as the evaporator for liquid benzene. The hot plate was used for heating up the sand bath. Liquid 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.

#### **4.3.2.3 Oil Bath**

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

#### **4.3.2.4 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.

#### **4.3.2.5 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 4.4.

#### **4.3.3 Reaction procedure**

The hydroxylation of benzene with hydrogen peroxide was carried out by using a conventional flow shown in Figure 4.2 under the following condition atmospheric pressure.

**Table 4.4** Operating conditions for gas chromatograph

Gas chromatograph	SHIMADZU GC9A
Detector	FID
Packed column	GP 10% SP-2100
Carrier gas	N <sub>2</sub> (99.999%)
Injector temperature (°C)	250
Detector temperature (°C)	250
Initial column temperature (°C)	100
Initial hold time (min)	5
Program rate (°C/min)	10
Final column temperature (°C)	170
Final hold time (min)	15
Analyzed chemicals	Benzene and Phenol

The procedures are described in the detail below.

1) 0.5 g of catalyst powder, 40 ml of 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 sand bath of the evaporating system to 130°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 benzene to the evaporating system. Upon entering the hot spiral tube, the liquid benzene was evaporated immediately to gaseous benzene and was flushed to the reactor by using N<sub>2</sub> as the carrier gas.

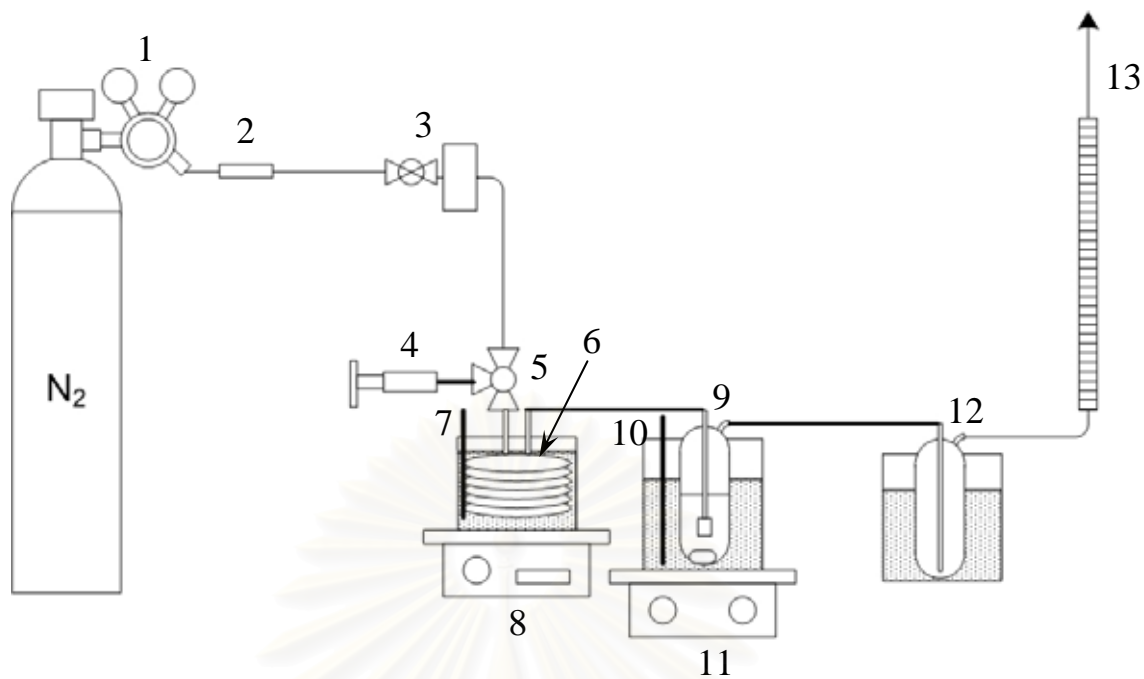
5) The gas mixture passes through the mixture containing the catalyst and hydrogen peroxide, where the hydroxylation of benzene reaction to phenol took place.

6) The next period, the equivalent liquid 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 15 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 phenol using a calibration curve (Appendix B).



**Figure 4.2** 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. Benzene Syringe    | 5. Three Way Connector | 6. Evaporator             |
| 7. Thermometer        | 8. Sand Bath           | 9. Reactor                |
| 10. Thermometer       | 11. Oil Bath           | 12. Gas Trap              |
| 13. Vent Gas          |                        |                           |

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## CHAPTER V

### RESULTS AND DISCUSSION

The results and discussion in this chapter are divided into two sections. The first section presents characterization of TS-1 catalyst and effects pretreatment on physicochemical properties of the catalyst. The second section reports catalytic hydroxylation reaction of benzene to phenol.

#### 5.1 Catalyst characterization

##### 5.1.1 XRF

Chemical compositions of the synthesized catalyst before and after the pretreatment were analyzed by x-ray fluorescence spectroscopy. Those results are presented in Table 5.1.

**Table 5.1** Chemical compositions ratio of synthesized TS-1 samples.

Sample No.	% wt. Si	% wt. Ti	Mole ratio of Si/Ti
Untreated Catalyst	30.1661	2.3918	12.6123
Pretreated Catalyst	30.8408	2.0047	15.3842

##### 5.1.2 BET

Surface areas and pore volume of each sample were measured by BET technique. The measured values of the fresh samples before and after the pretreatment are reported in Table 5.2.

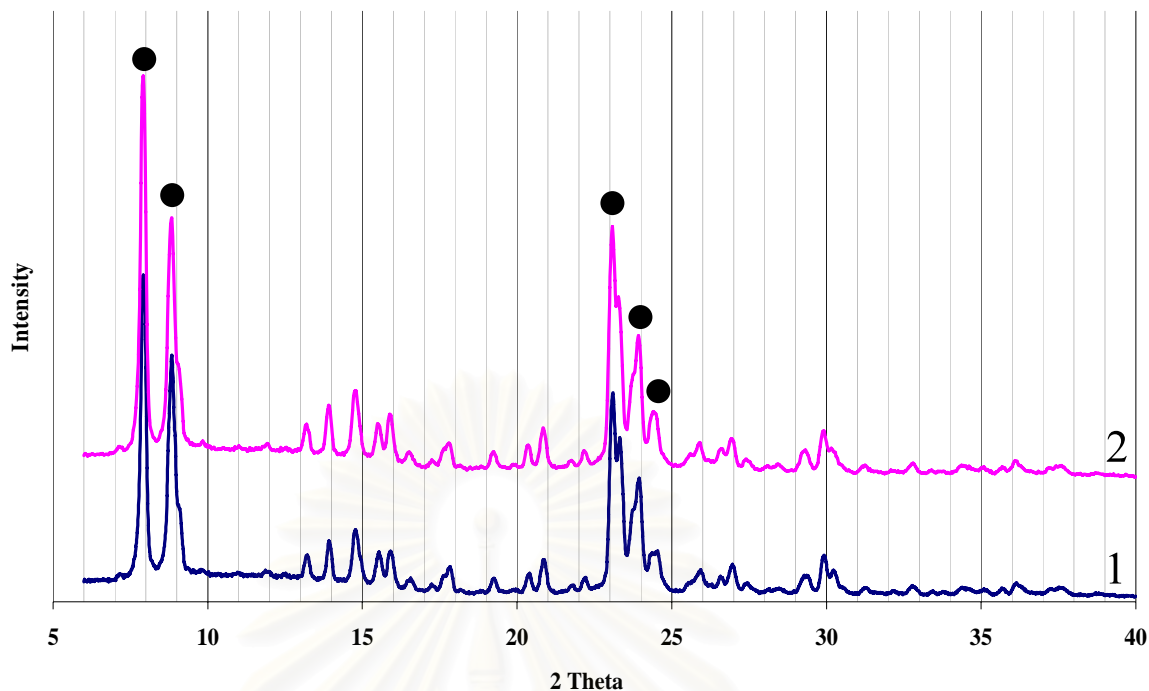
**Table 5.2** BET surface area of synthesized TS-1 samples

Sample no.	BET surface area (m <sup>2</sup> /g)	Pore size (Å)
Unpretreated Catalyst	281.3535	27.4194
Pretreated Catalyst	334.3492	25.0759

From Table 5.2, the surface areas indicate that the decrease amount of Ti lead to the increase of BET surface area. This is probably because the extra-framework titanium that covered pores of the catalyst was removed.

### 5.1.3 XRD

The crystallinity of the catalysts can be estimated by the intensity changes of five characteristic diffraction peaks ( $2\theta \approx 7.8^\circ, 8.8^\circ, 23.1^\circ, 23.8^\circ$  and  $24.4^\circ$ ) of the MFI zeolite. The results of Figure 5.1 show that all the samples behave the typical MFI structure. They have no peak at  $2\theta \approx 25.3^\circ$ , represents the anatase TiO<sub>2</sub> 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<sub>3</sub>.

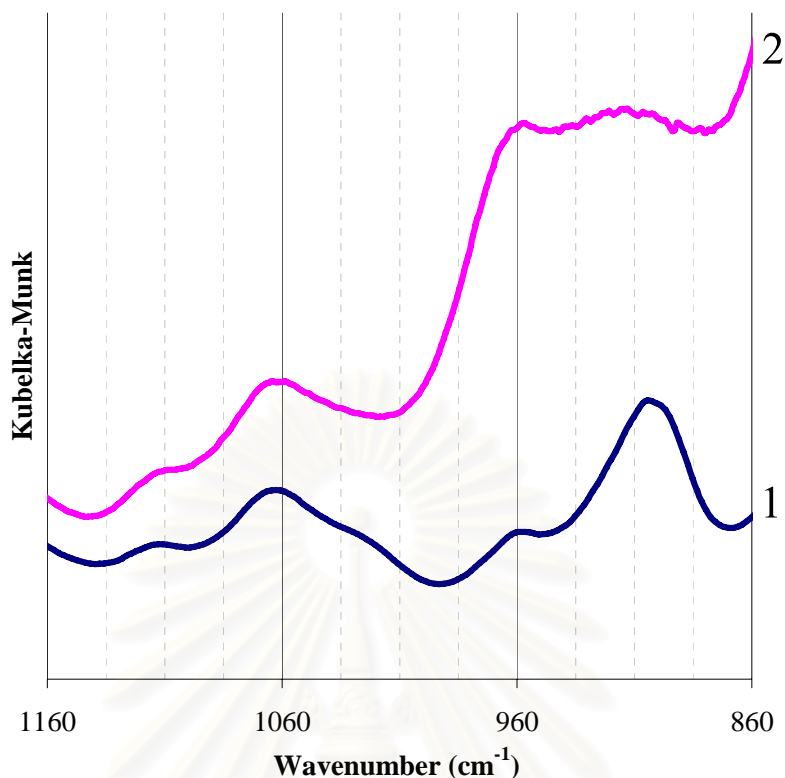


**Figure 5.1** XRD patterns of the TS-1 (1) unpretreatment and (2) pretreatment with 5 M HNO<sub>3</sub>.

#### 5.1.4 FT-IR

In 2001, Li *et al.* displayed that the catalytic performance of TS-1 is related to the amount of Ti in the framework of zeolite. With the decrease in Si/Ti ratio in the gel, the 960 cm<sup>-1</sup> band in the FT-IR spectra, characterization of framework titanium atoms becomes stronger. It shows more titanium atoms which are incorporated into framework.

The IR spectrum (Figure 5.2) of the synthesized TS-1 catalyst shows the characteristic absorption band of tetrahedral Ti<sup>4+</sup> in the TS-1 framework at 960 cm<sup>-1</sup> (Pirutko *et al.*, 2001). After pretreatment with 5M HNO<sub>3</sub>, it is found that the peak at about 960 cm<sup>-1</sup> does not weaken, which shows framework titanium species had no been washed off by HNO<sub>3</sub>.



**Figure 5.2** FT-IR spectrum of the TS-1 (1) unpretreatment and (2) pretreatment with 5 M HNO<sub>3</sub>.

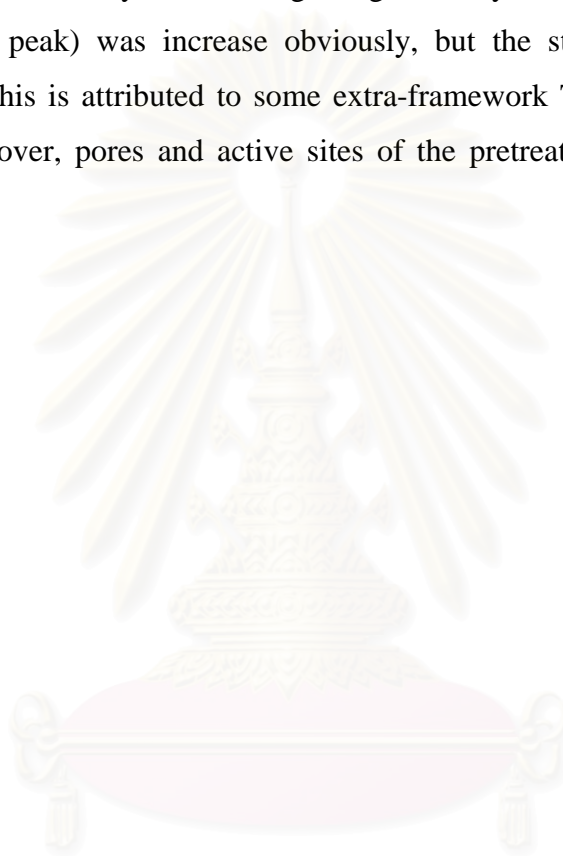
### 5.1.5 NH<sub>3</sub>-TPD

NH<sub>3</sub>-TPD was used to determine the strength and amount of the acid site of the catalysts. The results are shown in Figures 5.3-5.6 and Table 5.3. The deconvolution of the NH<sub>3</sub>-TPD spectrum are performed by using a freeware programme named “fityk”. The peak fitting process was carried out by finding the best fit of split-Gaussian peak(s). The amount of each acid site can be determined from the percentage of each component peak and the total amount of ammonia desorps. The results which are calculated from the raw data are showed in appendix C.

It is found that the NH<sub>3</sub>-TPD profile of the unpretreated catalyst can be deconvoluted into two main peaks. The first peak, will be named here “the weak acid site”, appears about 145°C. The second peak, will be named here “the strong acid site”, appears about 240°C. After pretreatment with 5M HNO<sub>3</sub>, it is found that the

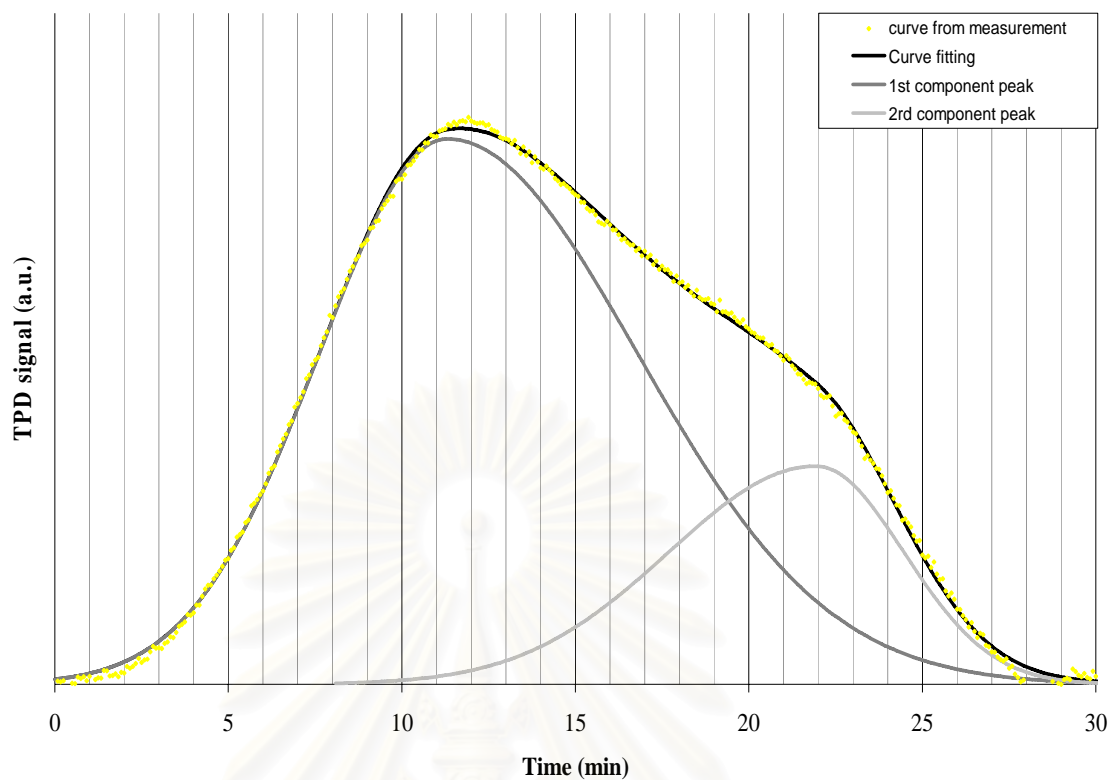
profile can not be separated. The only peak which is the weak acid site appears about 142°C.

The results of samples showed in Table 5.3 indicate that the quantities of the acid site. After the catalyst was pretreated with the aqueous solution of 5M HNO<sub>3</sub>, the acid strength (which can be determined from the location of the peak) on the surface of the TS-1 catalyst was changed significantly. The amount of acid site (the area under the peak) was increase obviously, but the strong acid site peak was disappeared. This is attributed to some extra-framework TiO<sub>2</sub> and impurities to be removed. Moreover, pores and active sites of the pretreated catalyst were increase importantly.

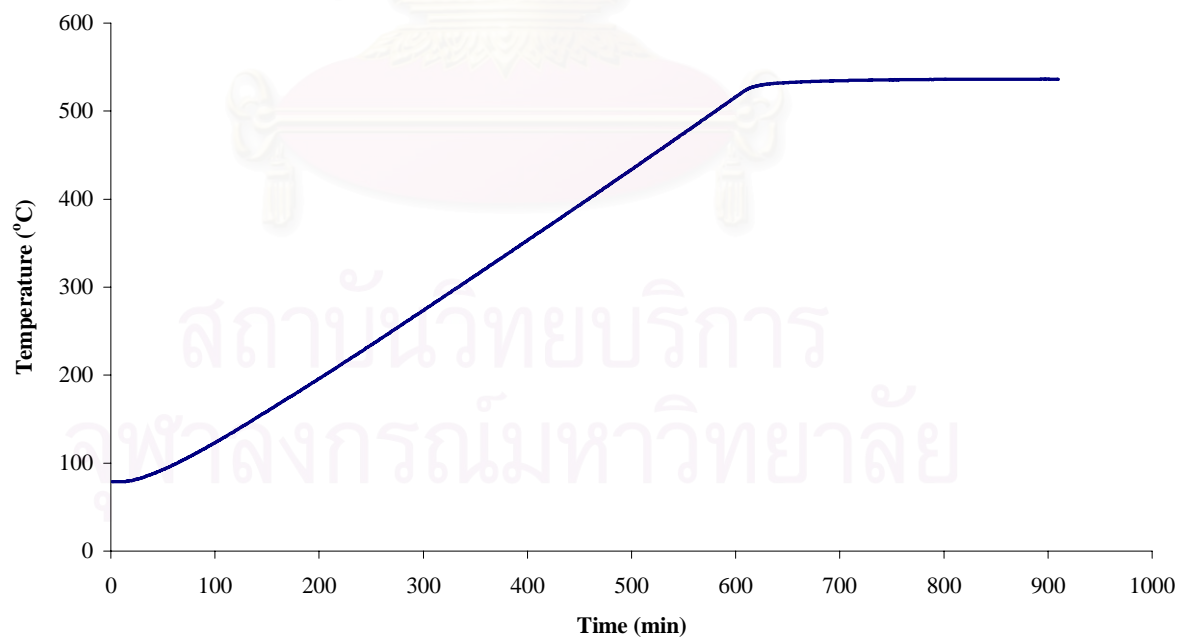


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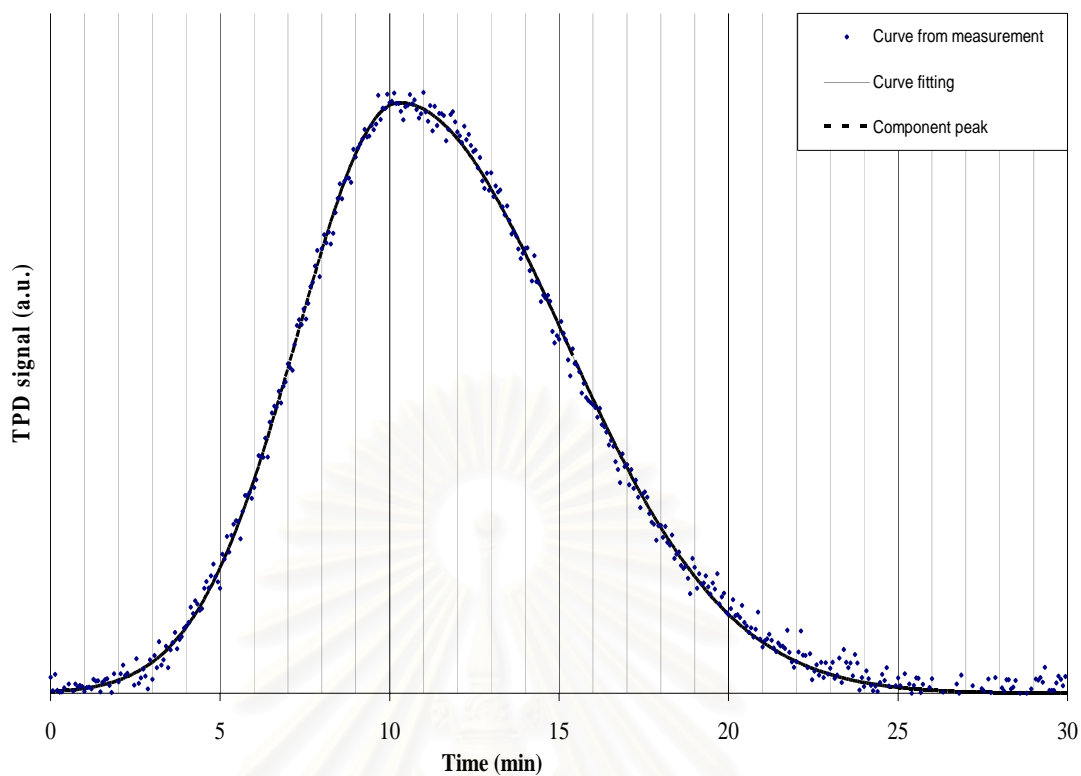




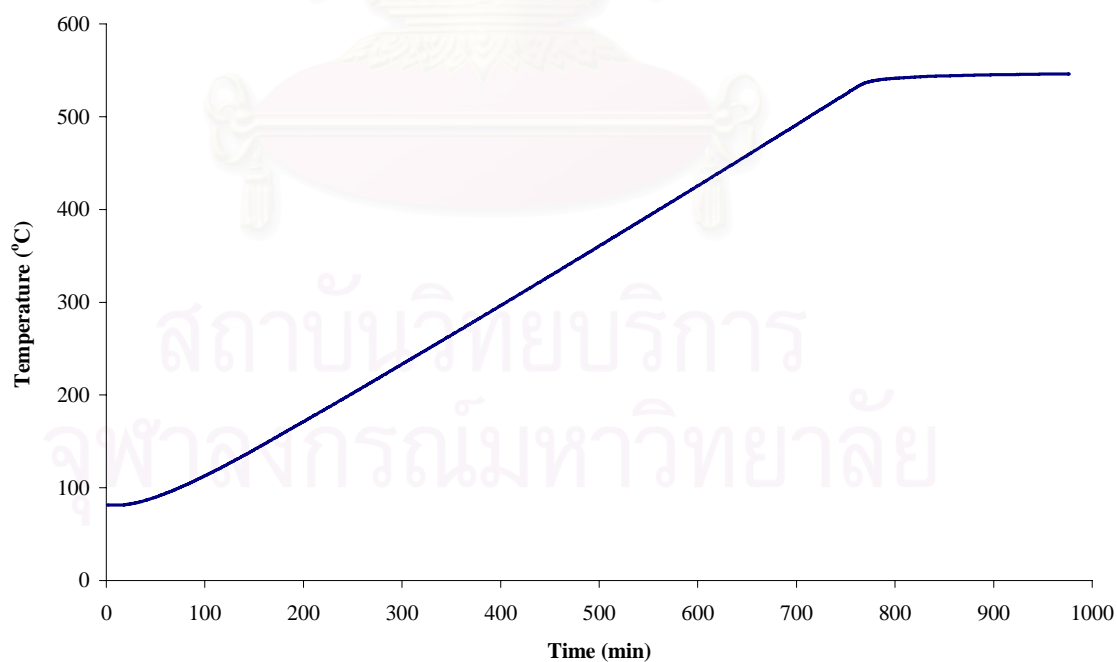
**Figure 5.3** The data of peak fitting of the TS-1 unpretreatment.



**Figure 5.4** The relation of temperature and time of the TS-1 unpretreatment



**Figure 5.5** The data of peak fitting of the TS-1 pretreatment with 5 M  $\text{HNO}_3$ .



**Figure 5.6** The relation of temperature and time of the TS-1 pretreatment with 5 M  $\text{HNO}_3$

**Table 5.3** Data of acid quantities and acid strength

<b>Sample</b>	<b>Temperature (°C)</b>	<b>Acid site (<math>\mu\text{mol/g}</math>)</b>	<b>Total (<math>\mu\text{mol/g}</math>)</b>
Unpretreated catalyst	145	99.2978	158.2600
	240	59.1764	
Pretreated catalyst	142	200.9981	200.9981



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## 5.2 Catalytic reaction

This section reports the effect of the hydroxylation of benzene to phenol over TS-1 catalysts pretreated with  $\text{NH}_3$  solution. The effect of benzene feeding procedure, reaction time and the amount of catalyst are discussed in sections 5.2.1, 5.2.2 and 5.2.3 respectively.

### 5.2.1 The investigation of benzene feeding procedure

From the fact that benzene is a volatile organic compound which easily evaporated to gaseous phase. The use of conventional saturator to evaporate benzene and control the concentration of the gas mixture by adjusting the saturator temperature is difficult to do practically. To overcome this problem, the pulse injecting of liquid benzene and the evaporating system were used instead of the saturator. The feeding parameters such as the amount of benzene feeding per period and feeding frequency, the volume of benzene feeding per time and the feeding period were studied in sections 5.2.1.1, 5.2.1.2 and 5.2.1.3, respectively.

#### 5.2.1.1 The effect of the volume of benzene feeding per period and feeding frequency on the conversion of benzene.

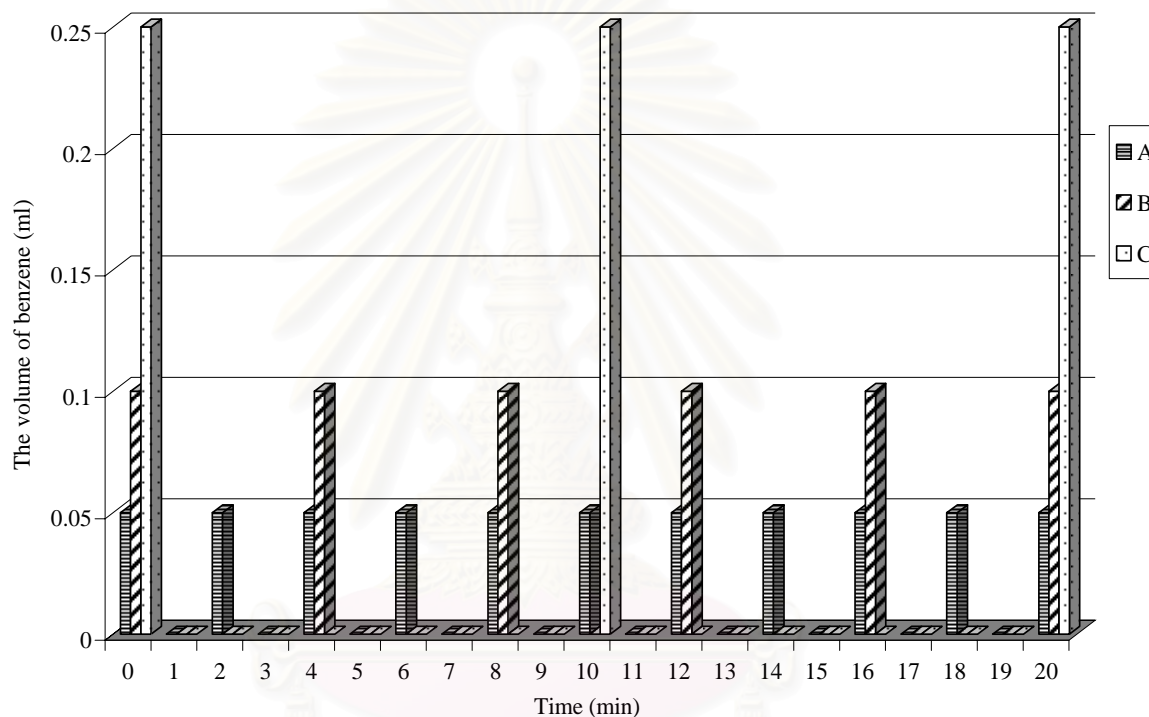
In this part, the effect of the volume of benzene feeding per period and feeding frequency was studied by fixing benzene feeding rate at 0.025 ml per minute. The overall volume of benzene feeding during each experiment was fixed at 3 ml and the reaction time was fixed at 2 hours. To imitate the continuous flow, small volume of benzene was pulse injected to the system in the certain frequency until all of benzene is completely fed. To keep the average benzene feeding rate at the constant value, both volume of benzene feeding per period and feeding frequency in each experiment were varied. 3 sets of experiment were performed (A-C) and the volume of benzene feeding per period and feeding frequency in each experiment was showed as follows:

Set A: The volume of benzene feeding is 0.05 ml in each 2 minutes

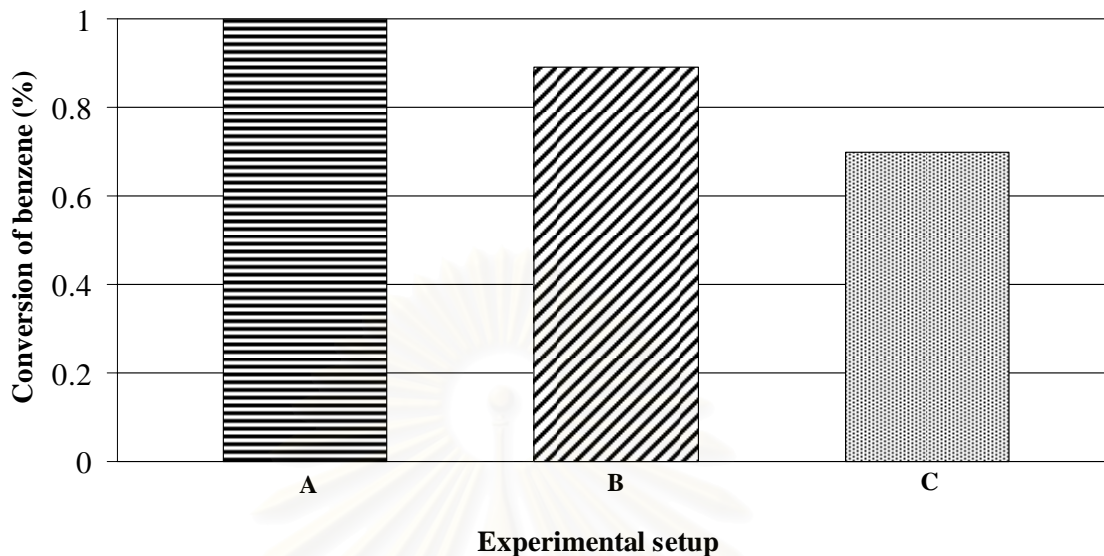
Set B: The volume of benzene feeding is 0.1 ml in each 4 minutes

Set C: The volume of benzene feeding is 0.25 ml in each 10 minutes

The diagram of the experiment is shown in figure 5.7 and the results of the study are shown in figure 5.8.



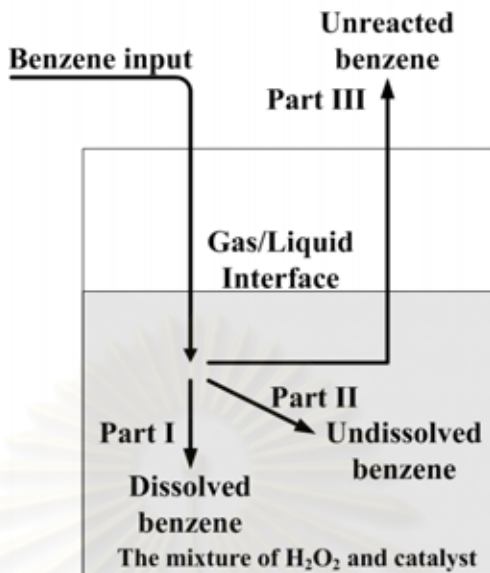
**Figure 5.7** The experimental diagram shows time of benzene injection of each method. (A: Injected benzene 0.05 ml in each 2 minutes, B: Injected benzene 0.1 ml in each 4 minutes, C: Injected benzene 0.25 ml in each 10 minutes)



**Figure 5.8** The effect of the amount of benzene feeding per period and feeding frequency on the conversion of benzene. (A: Injected benzene 0.05 ml in each 2 minutes, B: Injected benzene 0.1 ml in each 4 minutes, C: Injected benzene 0.25 ml in each 10 minutes)

Figure 5.8 illustrates that the conversion of benzene increased when the volume of benzene feeding in each period decreased while the feeding frequency increased (A). Only phenol product was observed for all of the experiment. The maximum conversion was achieved at 1% with 100% phenol selectivity for experimental set A. It may suggest from the results that feeding in small volume with frequent injection is better than feeding in large volume with fewer injections. High frequency with small volume of benzene feeding would produce a pseudo-continuous flow of benzene within the system in which the concentration of benzene in the gas mixture is almost constant. To explain the influence of benzene feeding on the conversion of benzene, the model for bubble flow reactor was proposed in figure 5.9.





**Figure 5.9** The model for hydroxylation of benzene in bubble.

In the model, the gaseous benzene which enters the reactor is separated into 3 parts; Part I dissolve in H<sub>2</sub>O<sub>2</sub>, Part II non-dissolve in H<sub>2</sub>O<sub>2</sub> and Part III leave the system without reacting. Benzene in Part I is benzene molecules that enter the reactor and dissolve in the H<sub>2</sub>O<sub>2</sub> phase. Benzene molecules in this part may further react with H<sub>2</sub>O<sub>2</sub> to form phenol product. Nevertheless, the amount of benzene in this part is very low due to the low solubility of benzene in water. Therefore, the hydroxylation reaction in this part is low. Benzene in part II is benzene molecules that enter to the reactor and stay in the H<sub>2</sub>O<sub>2</sub> phase in bubble form. The benzene bubble will float up from the bottom of the reactor to the gas/liquid interface. During the path way, benzene bubble will have an opportunity to interact with H<sub>2</sub>O<sub>2</sub> and the catalyst. The reaction will take place and the phenol product will be formed. The benzene molecules which do not react with H<sub>2</sub>O<sub>2</sub> will leave the system as propose in part III. The distribution of benzene among these 3 parts depends on the concentration and the flow rate of the benzene feed. Higher benzene concentration in the feed provides higher driving force for the solubility of benzene into the H<sub>2</sub>O<sub>2</sub> phase. The higher benzene concentration, however, also results in higher benzene loss via part II and part III. A higher feed flow rate enhances the solubility of

benzene into the  $\text{H}_2\text{O}_2$  phase by providing a better mixing. The higher feed flow rate, at the same time, results in more benzene loss via part II and part III.

From the results above, it seems that both amount of benzene feeding per period and frequency of benzene feeding affect the conversion of benzene. Therefore, the additional experiment was performed in order to investigate the effect of the amount of benzene feeding per period and the feeding frequency separately.

#### **5.2.1.2 Effect of the volume of benzene feeding per period**

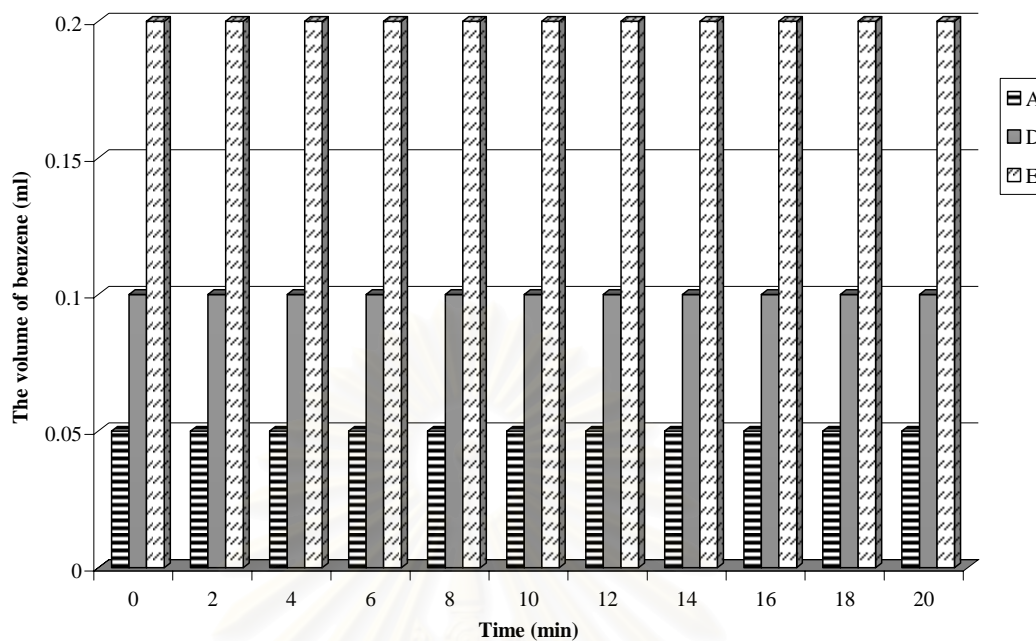
In this section, the effect of the volume of benzene feeding per period was investigated. The feeding frequency was fixed by feeding benzene portion in each 2 minutes. The overall volume of benzene feeding was fixed at 3 ml as the section 5.2.1.1. 3 sets of experiment were compared (A, C, D) as follows.

Set A: The volume of benzene feeding is 0.05 ml in each 2 minutes (The highest conversion from part 5.2.1.1)

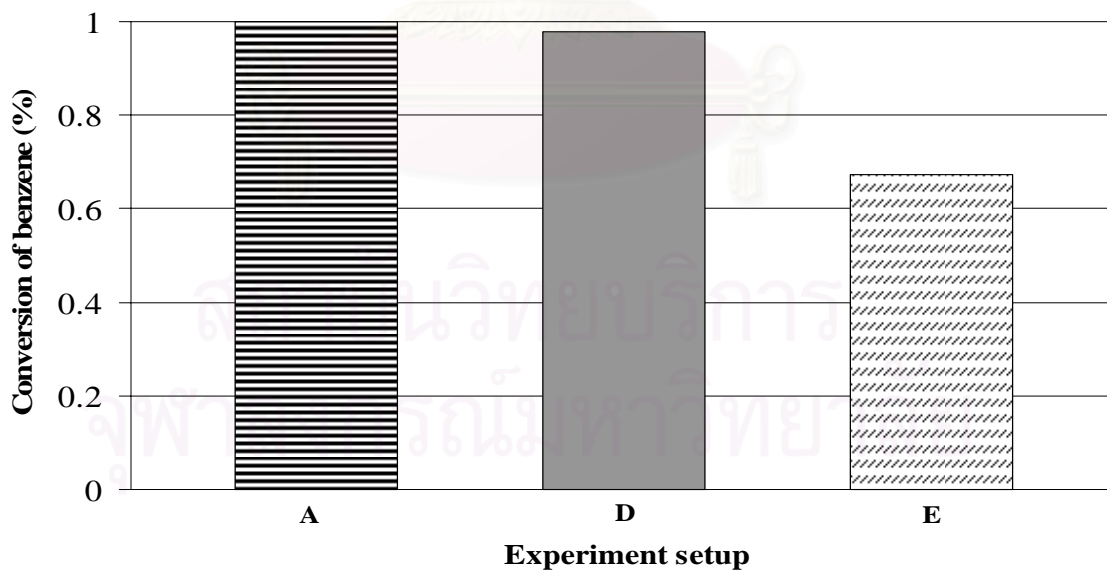
Set D: The volume of benzene feeding is 0.1 ml in each 2 minutes

Set E: The volume of benzene feeding is 0.2 ml in each 2 minutes

The injection was repeated until overall volume of benzene was completely fed. Owing to the volume of benzene injected in each period was difference at the same frequency feeding, therefore, the overall time of benzene feeding would be varied. To control this parameter, the reactor was left standing in its condition until the overall reaction time was 2 hours. The diagram of the desired experiment is shown in figure 5.10 and the results of this study are shown in figure 5.11.



**Figure 5.10** The experimental diagram studied the effect of the amount of benzene feeding per period. (A: Injected benzene 0.05 ml in each 2 minutes, D: Injected benzene 0.1 ml in each 2 minutes, E: Injected benzene 0.2 ml in each 2 minutes)



**Figure 5.11** The effect of the amount of benzene feeding per period on the conversion of benzene. (A: Injected benzene 0.05 ml in each 2 minutes, D: Injected benzene 0.1 ml in each 2 minutes, E: Injected benzene 0.2 ml in each 2 minutes)

Figure 5.11 shows that when the volume of benzene feeding in each period increased, the conversion of benzene decreased. This behavior could be explained by using model mentioned earlier in section 5.2.1.1 that when large amount of benzene was fed while the solubility rate of benzene did not increase proportionately to the volume of benzene injected in each injection, the benzene molecule which did not dissolve into the H<sub>2</sub>O<sub>2</sub> phase would leave the reactor (purpose as benzene molecule in part III from the model). In this case, the rate determining step could be the reaction of benzene to produce phenol. To better understand about the rate determining step, the average mole of phenol produced in each period was calculated by dividing overall mole of phenol produced by number of benzene injection time. This calculation was based on the assumption that mole of phenol produced in each period under the same condition was equal. The calculation data are shown in table 5.4.

**Table 5.4 The calculation data of average mole of phenol produced in each period**

<b>Benzene feeding in each period (ml/2minutes)</b>	<b>Number of benzene injection<sup>+</sup></b>	<b>Overall benzene conversion (%)</b>	<b>Overall mole of phenol produced (mole)</b>	<b>Average mole of phenol produced in each period (mole)*</b>
0.05 (A)	60	1.00	0.00034	$5.64 \times 10^{-6}$
0.1 (D)	30	0.97	0.00033	$1.10 \times 10^{-5}$
0.2 (E)	15	0.67	0.00023	$1.51 \times 10^{-5}$

<sup>+</sup> The number of benzene injection in each experiment was differenced because the volume of benzene feeding in each period was varied, but the overall volume of benzene feeding was fixed at 3 ml.

\* Average mole of phenol produced in each period was calculated by assuming that mole of phenol produced in each period under the same condition was equal. The value in table was obtained from dividing overall mole of phenol by number of benzene injection.

From table 5.4, the calculation data exhibit that the average mole of phenol produced in each period increased when the amount of benzene feeding increased. It might suggest that the increment of the amount of benzene feeding would increase the diffusion of benzene molecule to the catalyst active site resulted in the increasing of mole phenol produced in each period. Hence, the rate determining step should be the diffusion of benzene to the active site. However, the increment of phenol production was not in proportionate with the increment of benzene amount (i.e. between D and E, the amount of benzene increased two times but the phenol produced increased slightly). It seems that if further increase the amount of benzene, the phenol production would become steady. In this point, the rate determining step would change from the diffusion of benzene molecule to the reaction of benzene to phenol on the active site.

### **5.2.1.3 Effect of benzene feeding period**

To investigate the effect of feeding period, the experiments were performed as the same condition in section 5.2.1.2. In the study, the feeding period was varied and the volume of benzene feeding per period was fixed at 0.1 ml. 4 sets of experiments were showed as follow:

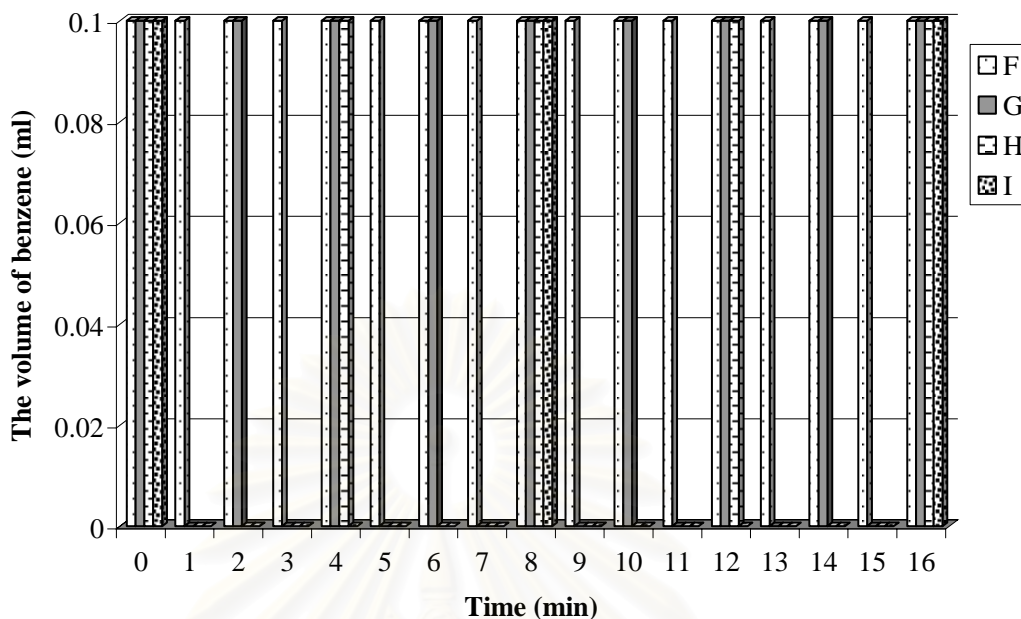
Set F: The amount of benzene feeding is 0.1 ml in each 1 minute.

Set G: The amount of benzene feeding is 0.1 ml in each 2 minutes.

Set H: The amount of benzene feeding is 0.1 ml in each 4 minutes.

Set I: The amount of benzene feeding is 0.1 ml in each 8 minutes.

The diagram of experiment studied the effect of benzene feeding rate is shown in figure 5.12

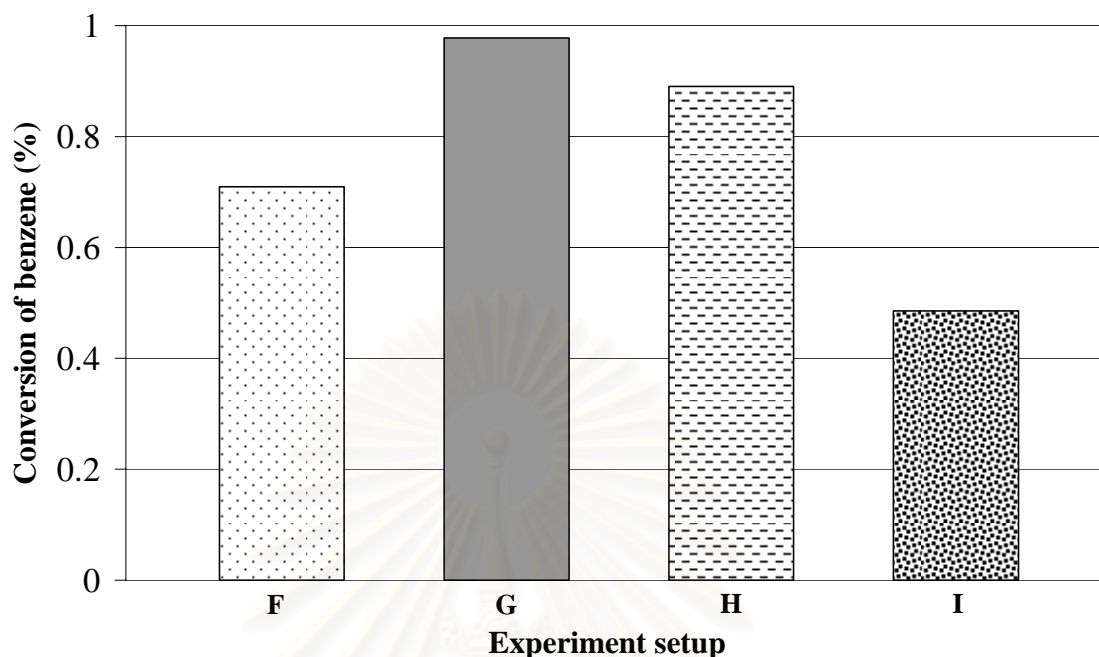


**Figure 5.12** The diagram of experiment studied the effect of benzene feeding rate. (F: Injected benzene 0.1 ml in each 1 minutes, G: Injected benzene 0.1 ml in each 2 minutes, H: Injected benzene 0.1 ml in each 4 minutes, I: Injected benzene 0.1 ml in each 8 minutes)

In every feeding period, the portion of benzene was injected to the system until the overall volume of benzene was 3 ml. The reaction was kept at 4 hours for every experiment. The results of this study are shown in figure 5.13.

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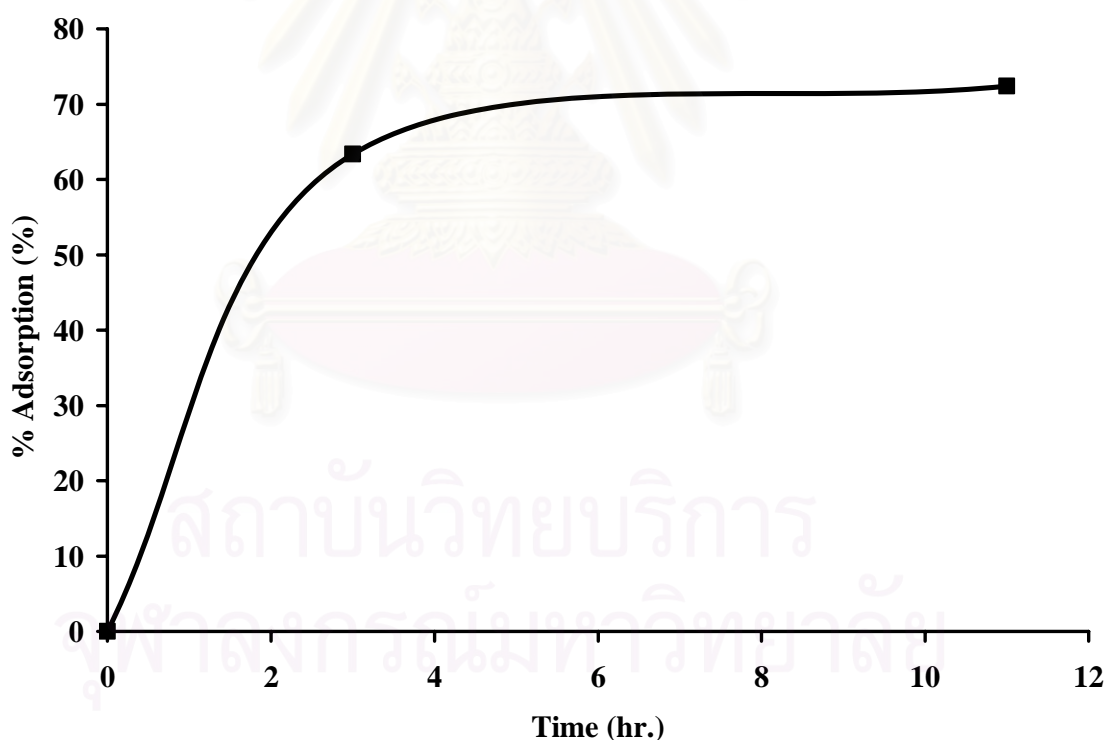




**Figure 5.13** The effect of benzene feeding period on the conversion of benzene (F: Injected benzene 0.1 ml in each 1 minutes, G: Injected benzene 0.1 ml in each 2 minutes, H: Injected benzene 0.1 ml in each 4 minutes, I: Injected benzene 0.1 ml in each 8 minutes)

From figure 5.13, it shows that the conversion increased when increased the feeding period from 1 to 2 minutes and then dropped continuously with further increasing benzene feeding period. The results of set F and G show that benzene feeding at higher frequency is less the benzene conversion than the feeding lower frequency. Consider the model from section 5.2.1.1, the benzene in reactor was separated in the 3 parts. When the volume of benzene was fed at very high frequency, the gaseous benzene in the reactor was more than enough. In part I, the amount of benzene was limited by solubility of benzene in water therefore the trend of the amount of benzene was constant. Due to the hydroxylation reaction was slowly, the excess benzene is unable to conduct the reactions in part II. The unnecessary benzene will leave the reactor as in part III. Hence, set F driving force is higher than the ability of reaction and benzene to dissolve in the  $H_2O_2$  phase cause to low benzene conversion.

Considering benzene feeding in our investigated region, the optimum condition was found at 2 minutes feeding period. When the feeding period was more than 2 minutes, it was observed that the conversion decreased. The decrement of conversion may be because of competitive adsorption between benzene reactant and phenol product on the catalyst surface. An amount of benzene must present in the  $H_2O_2$  phase to counter balance the adsorption of phenol, which is stronger adsorbed on the catalyst surface. If the concentration of benzene in the  $H_2O_2$  phase is allowed to low (i.e. the time interval between each injection is increased), more phenol will be adsorbed on the catalyst surface, thus, leaving less active site for the benzene. To better understand about the phenol adsorption into the catalyst, the expandable experiment is the effect of catalyst immerses the phenol solution. The phenol solution without catalyst and with catalyst were examined the disappearance of phenol in the solution.



**Figure 5.14** The adsorption of phenol of TS-1 catalysts.

Finally, these experiments could confirm that the pulse feeding method in our condition should make the appropriate flow of benzene in the reactor. The optimum feeding conditions which gave the highest conversion was the amount of benzene feeding at 0.1 ml injected in each 2 minutes.

### 5.2.2 Effect of reaction time

In this part, the effect of reaction time was studied by fixing the volume of benzene feeding per period at 0.1 ml and feeding period at 2 minutes. The overall reaction time was varied at 0.5, 1, 2 and 4 hours. The 4 sets of experiment were showed as follows:

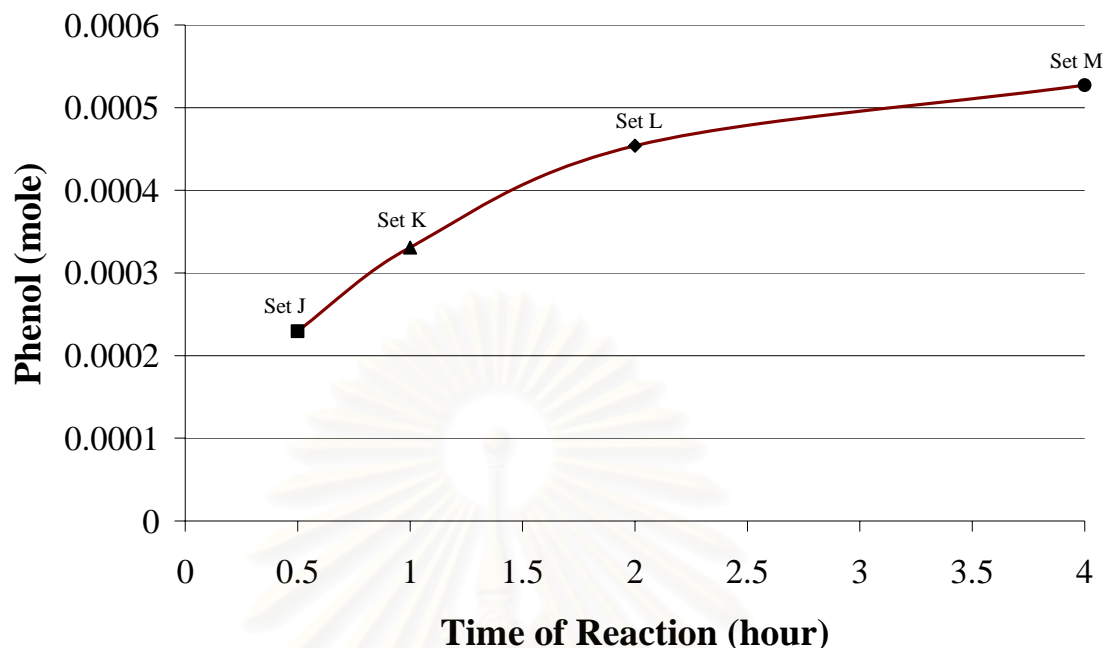
Set J: The benzene rate is 0.1 ml per 2 minutes and the reaction time is 0.5 hour.

Set K: The benzene rate is 0.1 ml per 2 minutes and the reaction time is 1 hour.

Set L: The benzene rate is 0.1 ml per 2 minutes and the reaction time is 2 hour.

Set M: The benzene rate is 0.1 ml per 2 minutes and the reaction time is 4 hour.

Mole of phenol produced in difference reaction time was measured in order to optimize the condition which gives the highest catalytic activity. The results of the study are shown in figure 5.15.



**Figure 5.15** The effect of reaction time on the mole number of phenol produced

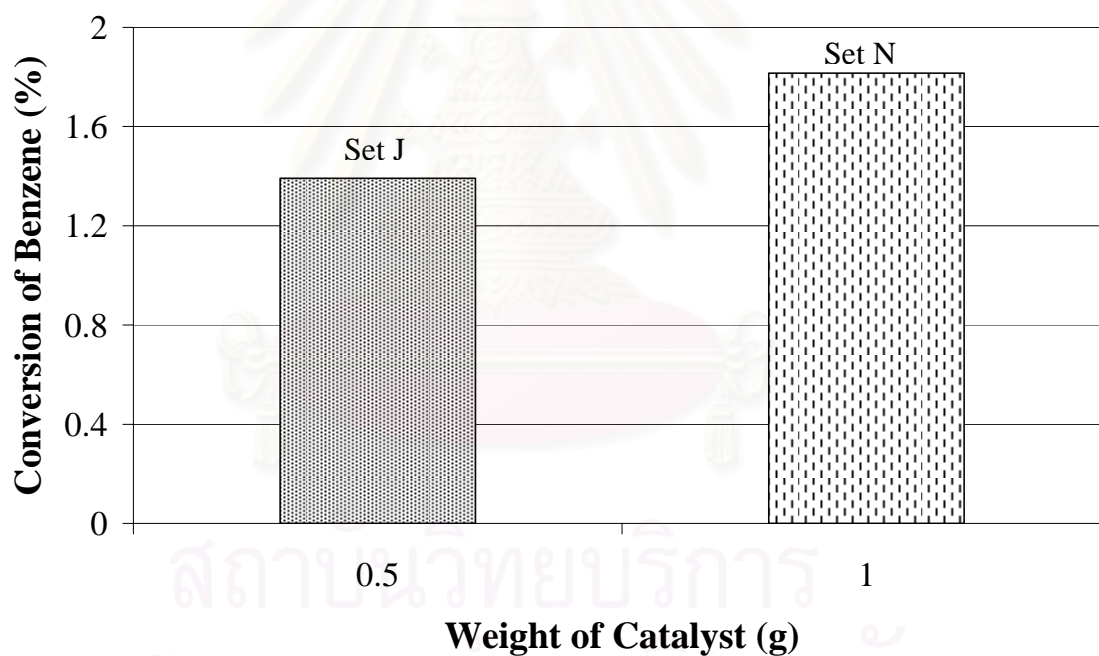
Figure 5.15 demonstrates that the amount of phenol increased when the experiments were left at the long time. Considering the reaction rate from the slope of graph, it was found that the slope of graph decreased slowly when the reaction time increased. It could predict that the trend of phenol produced would converge to constant value when reaction time was higher than 4 hours. After 4 hours, the catalyst might be inactive and would not be able to produce phenol anymore. As we described in part of the experimental (See in chapter IV) that the catalyst was merged into the reactor which contained 30% wt.  $\text{H}_2\text{O}_2$  solution. Thus, this phenomenon might be because of the competitive adsorption of water on the catalyst active site. The reaction would occur only when the catalyst was not fully absorbed by water molecules. When the catalyst was fully absorbed, benzene molecule would not have the chance to reach active site of the catalyst and the hydroxylation reaction would be limited.

### 5.2.3 Effect of the amount of catalyst

In this part, the effect of the catalyst amount was investigated. The benzene feeding rate was fixed at 0.1 ml injected in each 2 minutes and the reaction time was kept at 0.5 hour. The amount of catalyst was varied at 0.5 and 1 g. The sets of experiment were showed as follows:

Set J: The benzene rate is 0.1 ml per 2 minutes and the amount of catalyst is 0.5 g (the best benzene conversion from section 5.2.2).

Set N: The benzene rate is 0.1 ml per 2 minutes and the amount of catalyst is 1.0 g.



**Figure 5.16** The effect of the amount of catalyst on the conversion of benzene

The results of this study are shown in figure 5.16. It illustrates that the benzene conversion increased when the weight of the catalyst increased. At 1 gram of catalyst weight, the conversion reached 1.82% with 100% phenol selectivity. The increment of conversion might be because of the increasing of active site induces more opportunity for

benzene molecule to interact with  $\text{H}_2\text{O}_2$  and produce phenol on the active site. However, the increment of conversion did not in proportionate with the increment of catalyst amount (the conversion did not increase in two times by double increasing the catalyst amount). This might due to other effects which affect the catalytic activity such as the suspension of catalyst, the dispersion of benzene bubble in the reactor and the deactivation of catalyst. Considering figure 5.14, that shows the phenol adsorption in catalyst cause to vanish active site, is strongly support that the benzene conversion was not in proportionate with the increment of the catalyst amount.



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## CHAPTER VI

### CONCLUSIONS AND RECOMMENDATION

In the present research, the hydroxylation of benzene reaction in a bubble reactor was studied the effect of benzene feeding procedure, reaction time and the amount of catalyst. The conclusions emerged from all the experiments are summarized in section 6.1. Section 6.2 is given the recommendations for further study.

#### 6.1 Conclusions

1. The benzene conversion decreased when increased the volume of benzene feeding while feeding frequency decreased. Therefore, the injection of benzene into reactor should be decrease the volume of benzene feeding while increased feeding frequency in order to imitate the continuous flow.

2. The volume of benzene feeding in each period increased while the feeding frequency constant, the conversion of benzene decreased. However, the reaction rate remained constant or the reaction rate did not increase proportionately to the volume of benzene.

3. The pulse feeding method in our condition should make the optimum flow of benzene in the reactor. Because the higher benzene feeding made the excess benzene in reactor, that is unable to conduct the reaction. In contrast, the long feeding period made flow of benzene out of the continuous flow range.

4. The amount of phenol increased when the experiments were left at the long time. When reaction time was higher than 4 hours, the trend of phenol produced would converge to constant value.

5. The benzene conversion increased when the weight of the catalyst increased because of the increasing of active site. Moreover, the benzene conversion reached 1.82% with 100% phenol selectivity.

6. The model of the gaseous benzene which enters to the reactor is separated into 3 parts; Part I Dissolve in  $H_2O_2$ , Part II Non-dissolve in  $H_2O_2$  and Part III Leave the system without reacting. The reaction will take place in part I and part II.

## 6.2 Recommendations

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

1. Other alternatives of method for synthesized TS-1 catalysts including sources of Si, Ti, template and base solution should be further investigated.
2. Other acid solution for the pretreatment of TS-1 catalysts should be tried.
3. Other choices of manipulated variables such as: the reaction temperature; the concentration of  $H_2O_2$ ; the flow rate of carrier gas; the height of  $H_2O_2$  in reactor should be carrier out.
4. Comparison results between the experiment and the mathematical models are also recommended to investigate the behavior of system.

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**APPENDICES**

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## APPENDIX A

### DATA OF EXPERIMENTS

**Table A1** Data of experiment in each set of research.

Set of experiment	Volume of H <sub>2</sub> O <sub>2</sub> (ml)	Weight of catalyst (g)	Volume of benzene (ml)	Reaction time (hr)	Benzene temperature (°C)	N <sub>2</sub> flow (cc/min)	Reactor temperature (°C)	Feeding rate of benzene (ml/min)	Benzene conversion (%)
Set A	40	0.5	3	2	130	60	70	0.05ml/2min	1.00
Set B	40	0.5	3	2	130	60	70	0.1ml/4min	0.89
Set C	40	0.5	3	2	130	60	70	0.25ml/10min	0.70
Set D	40	0.5	3	2	130	60	70	0.1ml/2min	0.98
Set E	40	0.5	3	2	130	60	70	0.2ml/2min	0.67
Set F	40	0.5	3	4	130	60	70	0.1ml/1min	0.71
Set G	40	0.5	3	4	130	60	70	0.1ml/2min	0.98
Set H	40	0.5	3	4	130	60	70	0.1ml/4min	0.89
Set I	40	0.5	3	4	130	60	70	0.1ml/8min	0.49
Set J	40	0.5	1.5	0.5	130	60	70	0.1ml/2min	1.36
Set K	40	0.5	3	1	130	60	70	0.1ml/2min	0.98
Set L	40	0.5	6	2	130	60	70	0.1ml/2min	0.67

**Table A1(cont.)** Data of experiment in each of set of research.

Set of experiment	Volume of H <sub>2</sub> O <sub>2</sub> (ml)	Weight of catalyst (g)	Volume of benzene (ml)	Reaction time (hr)	Benzene temperature (°C)	N <sub>2</sub> flow (cc/min)	Reactor temperature (°C)	Feeding rate of benzene (ml/min)	Benzene conversion (%)
Set M	40	0.5	12	4	130	60	70	0.1ml/2min	0.39
Set N	40	1.0	1.5	0.5	130	60	70	0.1ml/2min	1.82

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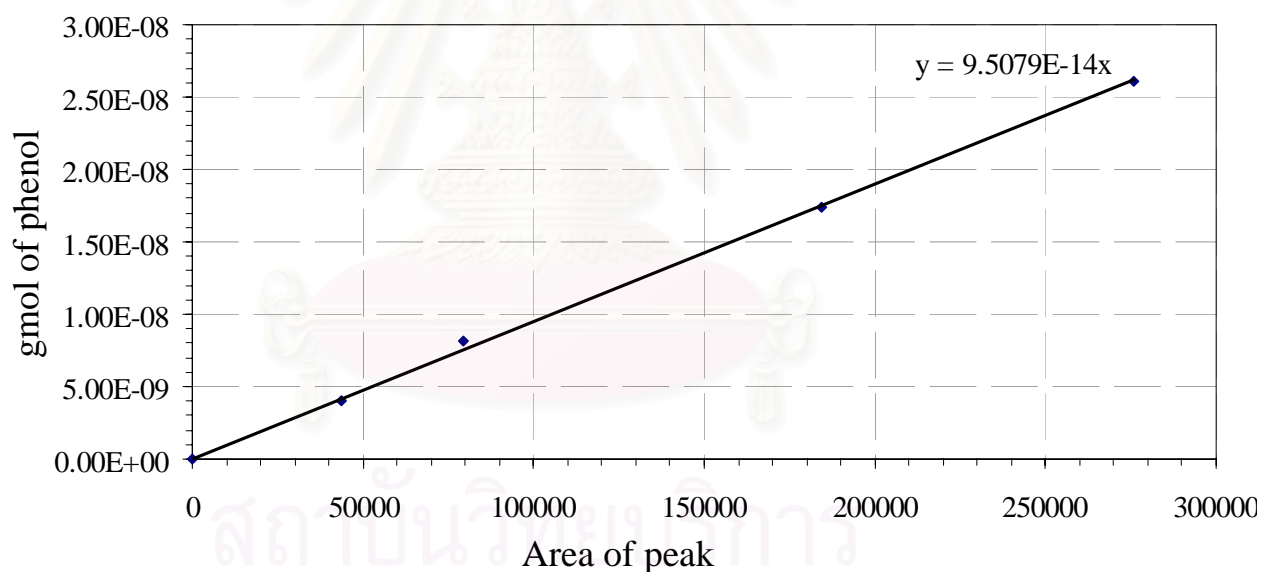
## APPENDIX B

### CALIBRATION CURVES

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

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 phenol is illustrated in the following figures.



**Figure B.1** The calibration curve of phenol.

## APPENDIX C

### DATA AND CALCULATION OF ACID SITE

#### C1. Calculation of total acid sites

Unpretreated catalyst sample, total acid site is calculated from the following step.

##### 1. Conversion of total peak area to peak volume

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

$$\begin{aligned}\text{Total peak volume} &= 77.5016 \times \text{total peak area} \\ &= 77.5016 \times 0.0210 \\ &= 1.6303 \text{ ml}\end{aligned}$$

##### 2. Calculation for adsorbed volume of 15% NH<sub>3</sub>

$$\begin{aligned}\text{adsorbed volume of 15\% NH}_3 &= 0.15 \times \text{total peak volume} \\ &= 0.15 \times 1.6303 \text{ ml} \\ &= 0.2445 \text{ ml}\end{aligned}$$

##### 3. Total acid sites 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 pretreated catalyst sample, 0.1007 g of this sample was measured, therefore

$$\begin{aligned} \text{Total acid sites} &= \frac{0.2445 \text{ ml} \times 101.325 \text{ Pa}}{\left(8.314 \times 10^{-3} \frac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}}\right) \times 298 \text{ K} \times (0.1007 \text{ g})} \\ &= 99.2978 \mu\text{mol H}^+/\text{g} \end{aligned}$$

## C2. 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, Untreated catalyst sample sample, the ratio of each acid site on catalyst surface is calculated from the following equation.

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

From figure 5.13., 1<sup>st</sup> peak area and 2<sup>nd</sup> peak area are equal to 0.0210 and 0.0126, respectively.

$$\begin{aligned} \text{The ratio of weak acid} &= \frac{0.0210}{0.0210 + 0.0126} \times 100 \% \\ &= 62.50 \% \end{aligned}$$

$$\begin{aligned} \text{therefore, the ratio of strong acid} &= 100 - 62.50 \% \\ &= 37.50\% \end{aligned}$$

## APPENDIX D

### THE DATA OF X-RAY FLUORESCENCE (XRF)

#### D1. XRF Raw Data of Table 5.1

Sample: TS-1 Batch4  
Fri 9/29/2006 at 8:26:04 AM  
Method Name: 493214-3105

FCD Name

- 1 Medium Elmts - Liquids
- 2 V. Light Elmts - Liquids

FCD LT,s Zero FWHM Gain

- 1 40 -0.8 121.1 100.01
- 2 40 -0.5 89.2 100.01

Total: 29.16% (Normalised to 100%)

El Line	Concentration	+/- Err	Fit	Intensity
TiO2K	9.31 Wt %	0.10	2.3	638.9
Fe2O3Ka	0.22 Wt %	0.01	1.7	74.8
Cu2OKa	148 ppm	1.57E-3	6.3	17.6
ZnO Ka	200 ppm	1.43E-3	1.4	29.9
ZrO2Ka	108 ppm	1.52E-3	0.2	94.0
SiO2K	88.30 Wt %	0.19	46.7	15128.4
SO3 K	2.13 Wt %	0.04	6.8	497.6

**Figure D.1** Raw data of the untreated TS-1 catalyst.

Sample: TS-1 Pre4  
Fri 9/29/2006 at 8:17:43 AM  
Method Name: 493214-3105

FCD Name

- 1 Medium Elmts - Liquids
- 2 V. Light Elmts - Liquids

FCD LT,s Zero FWHM Gain

- 1 40 -0.9 121.0 100.01
- 2 40 -0.5 89.2 100.01

Total: 29.97% (Normalised to 100%)

El Line	Concentration	+/- Err	Fit	Intensity
TiO2K	7.82 Wt %	0.09	1.5	641.1
Fe2O3Ka	1644 ppm	0.01	2.7	69.9
Cu2OKa	162 ppm	1.32E-3	4.3	23.9
ZnO Ka	865 ppm	2.11E-3	1.6	160.5
ZrO2Ka	91 ppm	1.22E-3	0.5	97.6
SiO2K	90.47 Wt %	0.19	43.0	16138.5
SO3 K	1.43 Wt %	0.04	3.3	341.2

**Figure D.2** Raw data of the pretreated TS-1 catalyst.



## APPENDIX E

### CALCULATION OF BENZENE CONVERSION

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

Activity of the catalyst performed in term of benzene conversion. Benzene conversion is defined as overall mole of phenol with respect to overall mole of benzene feeding.

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

Where overall mole of phenol can be measured as follows:

$$\begin{aligned} & \text{Overall mole of phenol} \\ &= \frac{\text{Mole of phenol} \times \text{Total volume of solution before injection into GC-9A}}{\text{Volume of injection into GC-9A}} \quad (\text{D2}) \end{aligned}$$

Where mole of phenol can be measured employing the calibration curve of phenol in figure B.1, appendix B.,i.e.,

$$\begin{aligned} \text{Mole of phenol} &= ((\text{area of phenol peak from integrator plot on GC-9A}) \\ &\quad \times 9.5079 \times 10^{-14}) \quad (\text{D3}) \end{aligned}$$

Where overall mole of benzene can be measured as follows:

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

$$\text{Overall mole of benzene} = \frac{\text{Volume of benzene feeding} \times 0.88}{78.11} \quad (\text{D3})$$

## APPENDIX F

### MATERIAL SAFETY DATA SHEET OF BENZENE AND HYDROGENPEROXIDE

#### F1. 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.

## **F2. 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.

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

## VITA

Miss Panas Manit was born on October 1<sup>st</sup> 1983 in Bangkok, Thailand. She finished high school from Suankularb Witthayalai Nonthaburi School, Nonthaburi in 2001, and received the bachelor's degree of Chemical Engineering from Faculty of Engineering, Thammasat University in 2004. She continued her master's degree of Chemical Engineering at Chulalongkorn University in October, 2006.



สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย