ปฏิกิริยาออกซิเดชันแบบเลือกเกิดของเบนซีนบนตัวเร่งปฏิกิริยาที่มีส่วนประกอบของไททาเนียม-ซิลิกา

นางสาวพัชนี ฉ่ำมิ่งขวัญ

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SELECTIVE OXIDATION OF BENZENE OVER TITANIUM-SILICA BASED CATALYST

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A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Engineering Program in Chemical Engineering
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พัชนี ฉ่ำมิ่งขวัญ : ปฏิกิริยาออกซิเดชันแบบเลือกเกิดของเบนซีนบนตัวเร่งปฏิกิริยาที่มีส่วนประกอบของไทเทเนียม-ซิลิกา (SELECTIVE OXIDATION OF BENZENE OVER TITANIUM-SILICA BASED CATALYST) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร. ธราธร มงคลศรี, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม : PROF. WOLFGANG F. HOELDERICH, Dr. rer. nat. และ ดร. พรสวรรค์ อัศวแสงรัตน์, 110 หน้า

งานวิจัยนี้ได้ทำการศึกษาปฏิกิริยาออกซิเดชันของเบนซีน เพื่อเลือกเกิดเป็นฟีนอลโดยใช้ไฮโดรเจนเปอร์ออกไซด์เป็นตัวออกซิไดซ์ บนตัวเร่งปฏิกิริยาที่มีส่วนประกอบของไทเทเนียม-ซิลิกา ได้แก่ Ti-MCM-41, TS-1 และ TS-PQ^{TM} (ชื่อภายใต้ลิขสิทธิ์ของบริษัท PQ Corporation) ตัวเร่งปฏิกิริยาทั้งหมดที่ใช้ในการทดลอง ได้ถูกนำมาวิเคราะห์คุณสมบัติทางฟิสิกส์ ด้วยเทคนิค XRD, BET, DRUV-Vis, FT-IR และ SEM จากการศึกษาในเบื้องต้นพบว่า ตัวเร่งปฏิกิริยา TS-PQ^{TM} มีความว่องไวต่อปฏิกิริยาการออกซิเดชันแบบเลือกเกิดของเบนซีนมากที่สุด เมื่อเปรียบเทียบกับตัวเร่งปฏิกิริยาอื่นๆ ที่ใช้ในงานวิจัย ความว่องไวของตัวเร่งปฏิกิริยา TS-PQ^{TM} คาดว่าน่าจะเกิดจากปริมาณพื้นที่ผิวที่มาก ปริมาตรของรูพรุนที่สูง ส่วนประกอบของเมโซพอร์ ตลอดจนความบกพร่องทางโครงสร้างของตัวเร่งปฏิกิริยา นอกจากนี้ยังได้มีการศึกษาผลกระทบของความดัน การเติมไฮโดรเจนเปอร์ออกไซด์ อุณหภูมิ ความเร็วในการกวน สัดส่วนโดยโมลระหว่างเบนซีนและไฮโดรเจนเปอร์ออกไซด์ ปริมาตรของน้ำ และปริมาณตัวเร่งปฏิกิริยา ที่มีผลต่อประสิทธิภาพในการเร่งปฏิกิริยาของ TS-PQ^{TM} จากการทดลองพบว่า ตัวเร่งปฏิกิริยา TS-PQ^{TM} มีประสิทธิภาพในการเลือกเกิดฟีนอลได้อย่างดีเยี่ยมในสภาวะที่ไม่รุนแรง เช่น ที่อุณภูมิ 70 องศาเซลเซียส ภายใต้ความดันบรรยากาศ

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PATCHANEE CHAMMINGKWAN : SELECTIVE OXIDATION OF BENZENE OVER TITANIUM-SILICA BASED CATALYST. THESIS PRINCIPAL ADVISOR : ASSOC. PROF. THARATHON MONGKHONSI, Ph.D., THESIS COADVISOR : PROF. WOLFGANG F. HOELDERICH, Dr. rer. nat., PORNSAWAN ASSAWASAENGRAT, D.Eng., 110 pp.

The selective oxidation of benzene to phenol using hydrogen peroxide as an oxidant was studied over the titanium-silica based catalyst such as Ti-MCM-41, TS-1 and TS-PQ^{TM} (the trade mark of PQ Corporation). These catalysts have been characterized using various techniques such as XRD, BET, DRUV-Vis, FT-IR and SEM. Under the preliminary studied conditions, TS-PQ^{TM} exhibited the highest catalytic activity among the studied catalysts. These findings can be correlated to enlarged BET surface, larger pore volume and higher amount of mesopores in the material as well as defects of the catalyst structure. The effects of pressure, H_2O_2 addition rate, reaction temperature, stirring speed, molar ratio of benzene/H_2O_2, volume of additional water and catalyst weight, on the catalytic performance of TS-PQ^{TM} were investigated. Under mild conditions, such as 70°C and atmospheric pressure, an excellent overall phenol yield could be achieved over TS-PQ^{TM}.

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Lastly, I would like to dedicate the achievement of my work to my family. Without their love, support, encouragement, and understanding, I do not know if I would be able to finish this work ever.

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

TEOS	Tetraethyl orthosilicate
TPAOH	Tetrapropyl ammoniumhydroxide
TNBT	Tetra-*n*-butyl titanate
IPA	Isopropyl alcohol
DIPB	Diisopropylbenzene
PIPB	Polyisoproplybenzene
DMPC	Dimethylphenyl carbinol
ASM	Alpha-methylstyrene
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
DRUV-Vis	Diffuse reflectant ultraviolet visible spectroscopy
FT-IR	Fourier transform infrared
GC	Gas Chromatography
ICP-AES	Inductive couple plasma atomic emission spectroscopy
SEM	Scanning electron microscopy

Symbols

$C_{H_2O_2,\,Org.}$	Hydrogen peroxide conversion to organic compounds (%)
$C_{H_2O_2}$	Total H_2O_2 conversion (%)
$C_{Benzene}$	Benzene conversion (%)
S_{Phenol}	Phenol selectivity (%)
$S_{1,4-Benzoquinone}$	1,4-Benzoquinone selectivity (%)
$S_{Catecol}$	Catechol selectivity (%)
$S_{Hydroquinone}$	Hydroquinone selectivity (%)
n_{Phenol}	Mole of phenol after reaction
$n_{1,4-Benzoquinone}$	Mole of 1,4-benzoquinone after reaction

$n_{Catecol}$	Mole of catechol after reaction
$n_{Hydroquinone}$	Mole of hydroquinone after reaction
n_{0, H_2O_2}	Initial mole of hydrogen peroxide
$n_{0, Benzene}$	Initial mole of benzene
$n_{fin., H_2O_2}$	Final mole of H_2O_2 in the sample analyzed by titration method
w_i	Weight of standard i in the sample
$M.W._i$	Molecular weight of standard i
V	Total volume of sample
W	Total weight of sample
m_i	Mole of standard i
M_i	Molar concentration of standard i
v_{inj}	Injection volume of sample to gas chromatography
n_i	Overall mole of product i in the sample
A_i	Peak area of product i
$Slope_i$	Slope from the correlated calibration curve

CHAPTER I

INTRODUCTION

Phenol is an important intermediate which has extensive applications in a wide range of products. More than 90% of phenol currently produced in industrial scale is based on the cumene route. This route includes three steps, forming the final products phenol and acetone. To reach the economy of such a process, the amount of phenol production depends on the acetone demand in the market, which is dependent upon the automobile, construction and electronics businesses. Other disadvantages of this conventional process are the use of hazardous sulfuric acid as catalyst for the decomposition of the intermediate cumene hydroperoxide and that the multi-step reaction needs a large amount of energy especially in the separation process.

To reduce the operation costs and energy consumption, a lot of research is focused on the one-step production of phenol by selective oxidation of benzene ring in order to avoid the co-production of acetone. This reaction is known as one of the most challenging oxidation reaction because of high stability of benzene ring. Using heterogeneous systems, both gas and liquid phase operations were intensively studied. Various oxidants such as nitrous oxide [Motz *et al*., 1997; Motz *et al*., 1998; Hoelderich *et al*., 2000; Kollmer *et al*., 2004a; Kollmer *et al*., 2004b; Tatlier *et al*., 2005; Centi *et al*., 2003; Häfele *et al*., 1997; Ivanov *et al*., 2006; Pirutko *et al*., 2002; Hensen *et al*., 2005], molecular oxygen or air [Kanzaki *et al*., 2004; Bahidsky and Hronec, 2005; Passoni *et al*., 1997; Mita *et al*., 2005; Castagnola *et al*., 2005], the mixture of oxygen/hydrogen [Miyake *et al*., 1995; Kuznetsova *et al*., 2005; Sato *et al*., 2005; Itoh *et al*., 2003 ; Laufer and Hoelderich, 2002], the mixture of oxygen/ammonium [Liptáková *et al*., 2000; Liptáková *et al*., 2004; Bahidsky and Hronec, 2004] and hydrogen peroxide [He *et al*., 2001; Bengoa *et al*., 1998; Bhaumik *et al*., 1998; Kumar *et al*., 1999; Tanev *et al*., 1994; Gao and Xu, 2006; Cho *et al*., 2005; Dubey and Kannan, 2005; Lemke *et al*., 2003; Thangaraj *et al*., 1990; Balducci *et al*., 2003; Bianchi *et al*., 2007] were investigated. Using nitrous oxide as oxidant has economic advantage only when nitrous oxide comes as by-product from the adipic acid production and is clean. Thereby selectivity for phenol of up to 99% at phenol yield of up to 35 % can be achieved [Motz *et al*., 1997]. In contrast, the use of molecular oxygen or air as oxidant, oxygen/hydrogen system and oxygen/ammonium system result in low conversion and quite often in low selectivity. Hydrogen peroxide seems to be an attractive oxidant, which can be applied in a green process under mild conditions. Numerous studies are reported on the hydroxylation of benzene over various catalysts using different co-solvents in order to homogenize the mixture of benzene and H_2O_2. However, only few studies reported the reaction under, the most preferable, solvent-free system [Bengoa *et al*., 1998; Bhaumik *et al*., 1998; Kumar *et al*., 1999] and the remarkable results have been obtained by using TS-1 as catalyst.

In fact that TS-1 catalyst has hydrophobic property. The more hydrophobic is the catalyst, the less affinity of H_2O_2 oxidant to adsorb on the surface. Moreover, it is believed that co-solvent is needed for a typical TS-1 catalyst which contains mainly isolated Ti^{4+} ion in tetrahedral lattice position, in order to help H_2O_2 molecule hydrolyzing Ti-O-Si bonds and generate lattice defects as an active site for the catalytic system [Halasz *et al*., 2003]. On the other hand, TS-1 catalyst which is distorted by non-isomorphously substituted titanium ion or other defects might activate H_2O_2 even in the absence of a co-solvent [Halasz *et al*., 2003].

PQ Corporation has developed the titanium-silica containing catalyst, denoting as TS-PQ^{TM} catalyst. Although, TS-PQ^{TM} has the MFI structure with titanium incorporated into framework similar to TS-1, but it does not show hydrophobic character as frequently has been reported for TS-1 [Halasz *et al*., 2005]. This property should improve the adsorption of H_2O_2 and favor the selective oxidation of bezene. Moreover, TS-PQ^{TM} does not contain only isolated tetrahedral Ti^{4+} ion in the lattice positions like TS-1 catalyst. The distorted structure of this catalyst should have a benefit for activating H_2O_2 in the solvent-free system. These differences in physical features have already been reported to have an influence on the catalytic performance for the oxyfunctionalization of n-hexane to the corresponding alcohols. [Halasz *et al*., 2003; Senderov *et al*., 2003].

Therefore, it was of great interest to find out if TS-PQ^{TM} catalyst resulted in a better catalytic performance for the selective oxidation of benzene to form phenol than the TS-1 due to the fact of the different physical features .The catalytic activity of TS-PQ^{TM} for the selective oxidation of benzene using H_2O_2 as oxidant in three phase slurry reactor system was studied and compared with TS-1. Beyond TS-1, the catalyst with mesopore structure and hydrophilic surface, Ti-MCM-41, was synthesized and compared.

The operation conditions in the selective oxidation of benzene over TS-PQ^{TM} catalyst were optimized. The research has been scoped as follows:

1) TS-PQ^{TM} catalyst was provided by PQ Corporation.

2) TS-1 and Ti-MCM-41 catalysts were prepared by hydrothermal method.

3) Characterization of TS-PQ^{TM}, TS-1 and Ti-MCM-41 catalysts by using the following techniques.

- Determination of bulk composition of Si/Ti by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES).

- Determination of crystal size of the catalyst by Scanning Electron Micrographs (SEM).

- Determination of specific area and pore volume by N_2 adsorption based on Brunauer-Emmett-Teller method (BET) and Barrett-Joyner-Halenda (BJH), average micropore diameter based on Horvath-Kawazoe.

- Determination of structure and crystallinity of the catalysts by X-ray Diffractrometer (XRD).

- Determination of incorporation of Ti atoms as a framework element by Fourier Transform Infrared Spectrometer (FT-IR).

- Determination of coordination of Ti atoms in framework by Diffuse-Reflectance Ultraviolet-Visible Spectroscopy (DRUV-vis)

4) Catalytic reactions in liquid phase selective oxidation of benzene at various reaction conditions to determine catalytic activity.

5) Investigation the stability of TS-PQ^{TM} catalyst.

This present work is organized as follows:

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

The previous and current productions of phenol in commercial scale as well as the alternative route of phenol production including the selective oxidation of benzene to phenol in one-step using various oxidizing agents and various catalysts and comments on previous work were ascribed in Chapter II.

Chapter III consists of catalyst preparation, catalyst characterization, catalytic reaction in liquid phase, the method of H_2O_2 decomposition study and the calculation of conversion and product selectivity.

The experimental results of the characterization of TS-PQ^{TM}, TS-1 and Ti-MCM-41 catalysts, and the selective oxidation of benzene reaction over these catalysts, including an expanded discussion, are described in chapter IV.

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

Finally, the GC standard preparation and calibration curves for product analysis, the sample of conversion and product selectivity calculation, calculation of required amount of solvent for homogenization the mixture, the data of the experiments which had emerged from this research and material safety data sheet of benzene, hydrogen peroxide and reaction products are included in appendices at the end of this thesis.

CHAPTER II

LITERATURE REVIEW

2.1 Historical route of phenol production

Phenol is an important intermediate which has extensive applications in a wide range of products. It is firstly discovered in coal tar as early as 1834. In quantity production, phenol ranks near the top of the list of synthetic aromatic compounds. One of the early uses of phenol is an antiseptic. In 2004, around 40% of phenol was used in the production of bisphenol A, followed by phenol formaldehyde resins at 30%. Furthermore, it is used as an intermediate for the production of caprolactam, alklyphenols, aniline and adipic acid.

The first commercial manufacture of phenol is the distillation from coal tar. The process could not be sustained for long because the energy required producing the quantities meant. Another route of the earlier synthetic process had ever been used is the sulfonation of benzene to benzenesulfonic acid, followed by the fusion of sodium hydroxide. This process produces large amount of waste such as sodium sulphite. For this reason, the process could not reach the good atom economic. The schematic of the sulfonation of benzene is shown in **Figure 2.1**.

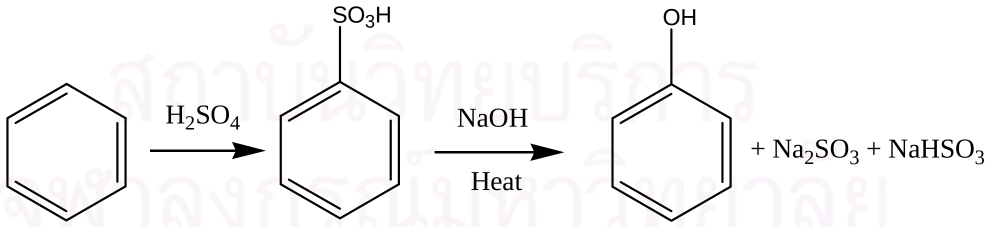


Figure 2.1 The sulfonation of benzene to produce phenol.

Two routes of phenol production are based on chlorination-based process. The first one, commercialized by Dow Chemical in 1924, is the direct chlorination of benzene to chlorobenzene before the chlorobenzene, intermediate, reacts with aqueous sodium hydroxide to produce phenol. Similar to the sulfonation process, this process is not longer in used because of the practical of the process depends strongly on the economics of the waste product. The schematic of the reaction is shown in **Figure 2.2.**

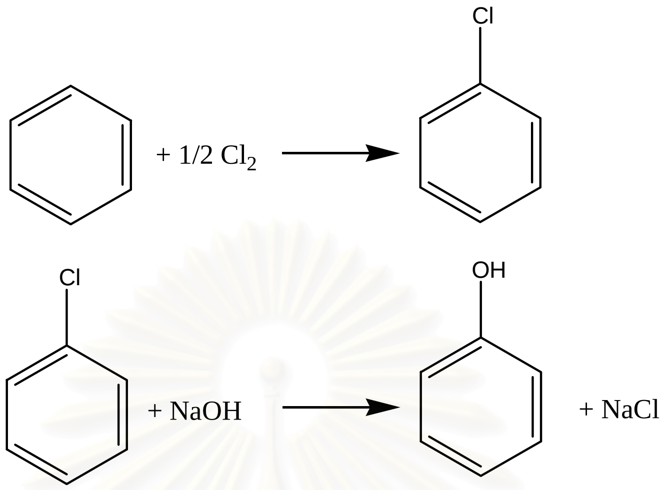


Figure 2.2 Chlorination-based process for phenol production by Dow Chemical in 1924.

The second clorolinated-based process is Raschig-Hooker process. The process involves the oxychlorination of benzene to provide chlorobenzene as an intermediate, follows by hydrolyzing of intermediate to give phenol and hydrogen chloride (hydrochloric acid). This process was extinguished because the high corrosion-resistant construction material which was required, brought about high capital investment. The schematic of Raschig-Hooker process is shown in **Figure 2.3**.

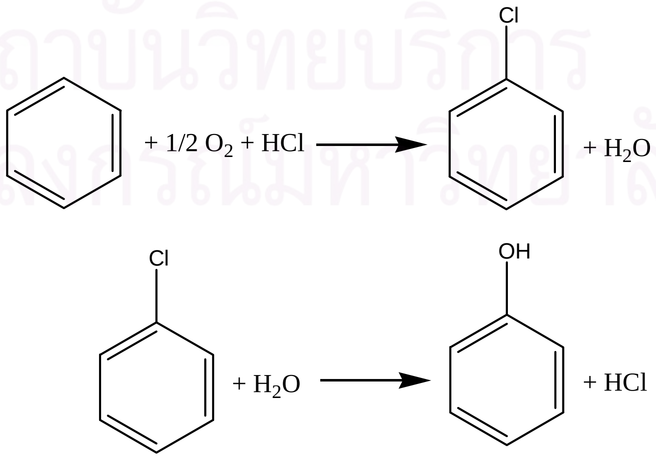


Figure 2.3 Raschig-Hooker Chlorination-based process for phenol production.

2.2 The production of phenol from cumene route

More than 90% of phenol production is currently based on cumene route. The main market for cumene is phenol in which more than 95% of cumene production goes into the production of phenol and its acetone byproduct. The whole process includes three steps, starting from the production of cumene from benzene and propylene, following by the oxidation of cumene with air to form cumene hydroperoxide. The final process is the cleavage of cumene hydroperoxide into phenol and acetone. The schematic of this three-step process is shown in **Figure 2.4**.

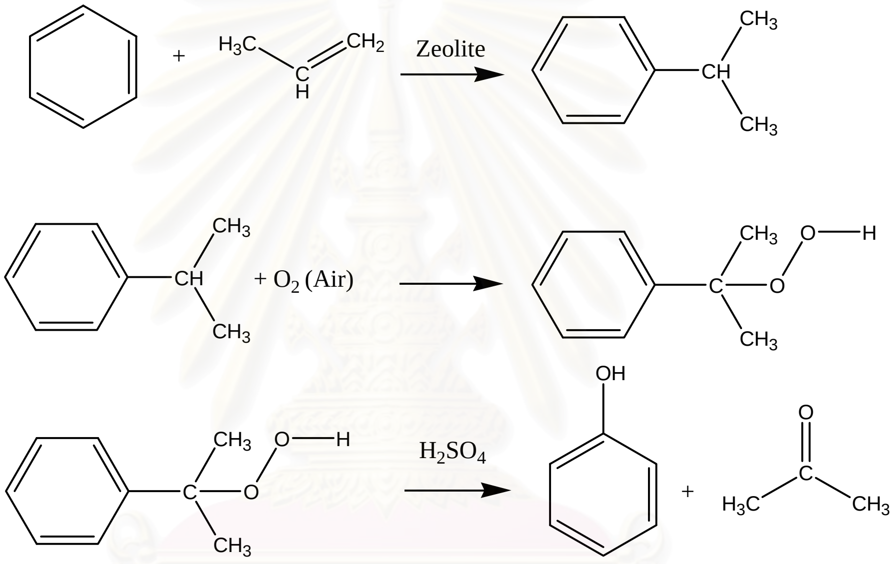


Figure 2.4 The production of phenol from cumene route.

2.2.1 Cumene production

Cumene is produced by alkylating benzene with refinery or chemical grade propylene. The reaction is catalyzed by acid catalyst and can be carried out in either the vapor or liquid phase. Pelletised phosphoric acid is usually used as a catalyst in vapor phase reaction. Phosphoric acid is very corrosive. The disposal of waste from this process can be a problem. Moreover, the catalyst can not be regenerated easily when it reaches the end of its useful life. In liquid phase, the Lewis acid aluminum chloride is used. It has advantage that the reaction can take place at 100°C under normal atmospheric pressure, but the corrosive waste is produced and the catalyst can not be easily regenerated. To awareness of the negative environmental impact, the new catalyst was developed to solve these problems and to improve economy. Currently, the zeolite-based catalyst is increasingly being used. This catalyst can be used without producing hazardous waste or acidic emission as well as it can be removed and regenerated for re-use. Cumene process technology is available on a commercial basis with four major suppliers namely, UOP LLC, Badger/Raytheon, and CDTECH.

2.2.1.1 The UOP's process

UOP catalytic condensation process is the world's leading technology for producing cumene. The process uses solid phosphoric acid as catalyst. This catalyst can yield benzene limiting at 95% because of the oligomerization of propylene and the formation of heavy alkylate by-products. To overcome the limitation, UOP began searching the new catalyst which is non-corrosive, regenerable, enhancement the yield of cumene and lowering the cost of production. The most promising catalyst based on β-zeolite has been selected and well known as QZ-2000^{TM} and QZ-2001^{TM} using in UOP Q-max process.

In the new UOP Q-Max process, benzene firstly reacts with propylene in the fixed-bed alkylation reactor to produce mainly cumene. The effluent from the alkylation reactor is sent to the depropanizer column to remove propane which entered the reactor from propylene feed. The bottom of depropanizer is sent to benzene column to separate benzene and recycle. The bottom, containing cumene and small amount of diisopropylbenzene, is sent to the DIPB column where diisopropylbenzene is separated from the cumene product, recycled to the transalkylation reactor and combined with additional benzene to form additional cumene. The QZ-2000^{TM} catalyst is used in both alkylation reactor and transalkylation reactor currently operating in seven Q-max units throughout the world. The excellent mass transfer properties minimize the formation of heavy by-product and produce superior cumene product quality at 99.7 wt.% yield. The newest QZ-2001^{TM} catalyst, commercialized in 2002, is used as the catalyst of choice in the alkylation reactor. It has twice stability of QZ-2000^{TM} catalyst in cumene alkylation service and currently uses in three Q-Max units throughout the world.

2.2.1.2 The Mobil/badger Process

The Mobil/badger process uses aluminum chloride catalyst in liquid phase to yield cumene. Recently, Mobil/Raytheon has developed a zeolite catalyst based on MCM-22. The reaction section employs both alkylation and transalkylation in fixed-bed reactor operating nearly isothermal condition. Benzene is combined with propylene and fed to the reactor. Mainly cumene product is formed at mild temperature and pressure with some of polyisoproplybenzene (PIPB) as by-product. The effluent is sent to benzene column to separate benzene before recycling to the reactor. The bottom stream is further sent to cumene to separate high purity cumene. PIPB is fractionated in a small PIPB column, recycled and combined with benzene to the reactor section to be transalkylated back to cumene.

2.2.1.3 The CDTECH process

This process has been developed by ABB Lummus and CR&L. The process is based on a Y-type zeolite operating in a catalytic distillation column reactor. The system combines reaction and fractionation in a single unit operation. The products from alkylation reaction are continuously removed from the reaction zone by distillation. These factors enhance the product purity and lower by-product formation.

2.2.2 Phenol production

Three main competitors for phenol production via cumene peroxidation include Sunoco/UOP, KBR and GE/Lummus. The main reactions of phenol and acetone produce via the oxidation of cumene to cumene hydroperoxide by air and the cleavage of cumene hydroperoxide to form phenol and acetone. The oxidation of cumene to cumene hydroperoxide proceeds via a free radical mechanism which is essentially auto-catalyzed itself. The reaction condition is carried out at the temperature range of 90-130°C and pressure 1-10 atmosphere. In the oxidation of cumene to cumene hydroperoxide, dimethylphenyl carbinol (DMPC) is the main oxidation by-product. The side reaction is minimized by optimization of the process conditions. In Sunoco/UOP process, DMPC is dehydrated by mineral acid to form alpha-methylstyrene (ASM) and further hydrogenated to form cumene before recycling back to feed stock or refining for sale as a product.

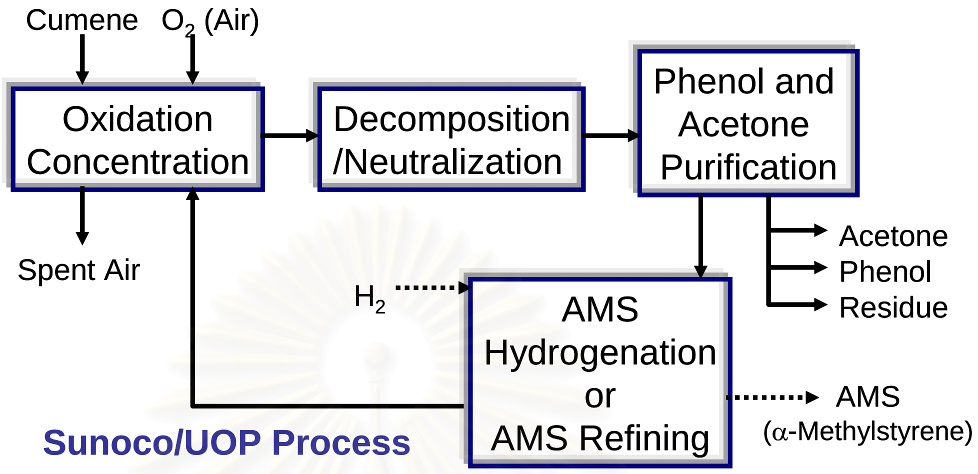


Figure 2.5 Sunoco/UOP Process.

2.3 Alternative method for phenol production

The phenol production from cumene route is currently used in the industrial process. This route includes three steps which the final products are phenol and acetone. Acetone is produced 0.28 kg per kg of phenol in this process. To reach the economic of process, the amount of produced phenol depends on the acetone's demand in the market which is strongly dependent on automobiles, construction and the electronics business. From 1996 to 2001, the growth of phenol was 1.8% while the growth of acetone was 0.9%. In the future, acetone may become waste of the process if its demand could not improve. Other disadvantages of this process are the hazardous intermediate, cumene hydroperoxide, and the multi-step reaction needs large amount of energy consumption especially in the separation process.

Toluene oxidation route is one alternative process for phenol production developed and operated by DSM in Boltlek, Netherland and also by Noveon Kalama in Washington, USA. In the process, phenol is produced from toluene in two-step reaction as shown in **Figure 2.6**. Toluene is rapidly oxidized to benzoic acid in the first step over cobalt salts. The operation conditions range from 1 atm to 10 atm and 130°C to 180°C. The second step is the oxidation of benzoic acid to form phenol. The process produces no by-product acetone and fewer impurities make it lesser dependent on the demand of acetone’s market. However, the whole process uses energy more than cumene route 3 to 4 times, and so it is not wildly in used. In 2004, DSM has transformed into a specialty company and decided to focus on intermediates and derivatives. Therefore, the production of phenol form this route is terminated.

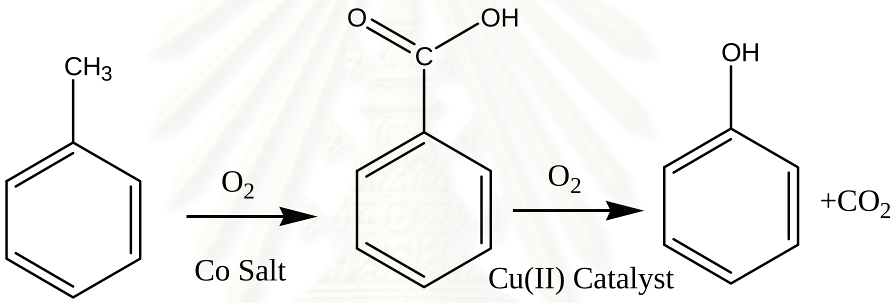


Figure 2.6 The production of phenol from toluene oxidation route.

To solve the problem of acetone by-product, Mitsui has developed a technology to use acetone by-product in propylene production. Propylene is then used as a raw material for cumene production as shown in Figure 2.7.

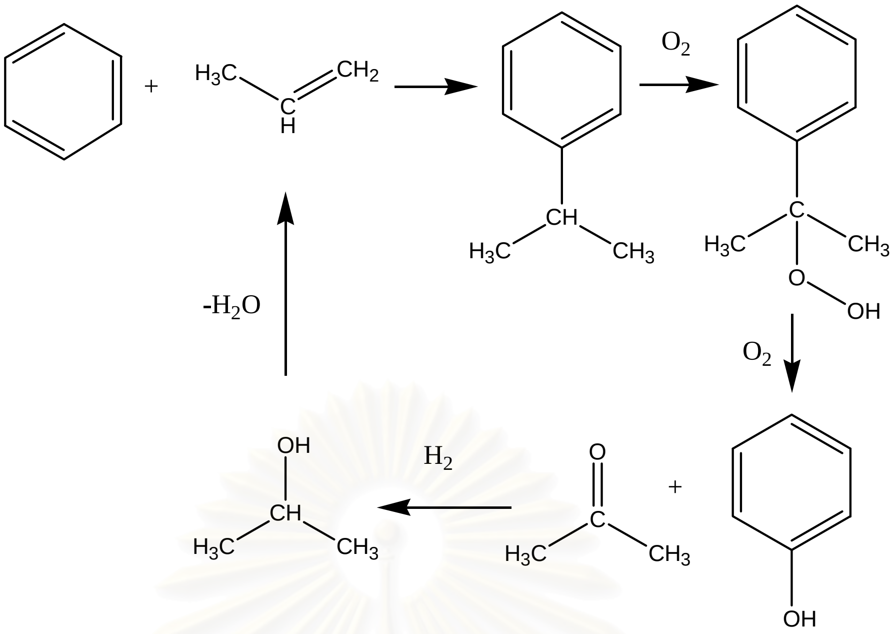


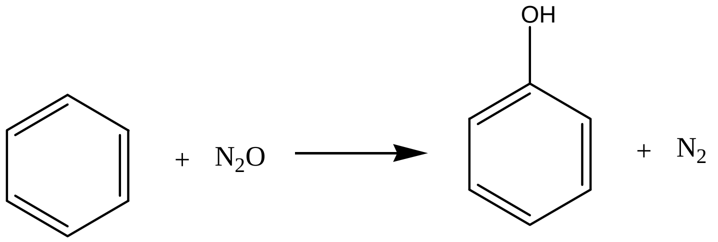
Figure 2.7 Mitsui’s acetone recycling technology in phenol manufacturing.

2.4 The selective oxidation of benzene to phenol

The one-step process, selective oxidation of benzene to phenol is currently interested for the industrial and academic research. The driving force of attention comes from its advantages of this route, the reduction in number of process steps, the elimination of waste by products, the reduction of energy consumption and the development of new process. The part is intended to review the results of the selective oxidation of benzene to produce phenol in one-step process over various catalysts. The review is divided into sub-topic considering the oxidant which was used in the studies.

2.4.1 The selective oxidation of benzene using nitrous oxide

Direct oxidation of benzene to phenol using nitrous oxide has been developed in the last 20 year. The reaction of benzene and nitrous oxide to form phenol is shown below;



(2.1)

The first study reported the use of V_2O_5/SiO_2 catalyst. 11% benzene conversion was achieved with 45% phenol selectivity [Iwamoto *et al.*, 1983]. Among the heterogeneous catalyst system, Fe-based zeolites with MFI structure, including ZSM-5 and silicalite, have been the major research focus. It was proved as the active catalysts for the selective one-step insertion of the hydroxyl group into aromatic ring. Iron in the zeolite structure can be formed in different form such as isolated ions isomorphously substituted in the MFI framework, ions in cation-exchange positions, iron complexes of low nuclearity in extraframework positions, iron oxide nanoparticles of < 2 nm size in the micropores and large Fe oxide particles (2 nm to 25 nm) located at the external surface of zeolite crystals [Yuranov *et al.*, 2004]. However, only a small part of the total iron is usually active in the reaction and the structure of active site is still in the subject of controversy. Initially, iron usually exists in zeolites in a trivalent state Fe^{3+}. The catalyst has to be activated in order to transfer trivalent state iron into the active form by high temperature calcination in steam, vacuum or inert atmosphere. Some researchers have purposed that the catalytic activity of these catalysts is related to the presence of iron which forms into the specific sites in the zeolite matrix called α-sites under high temperature treatment [Panov *et al.*, 1998]. The unique property of α-sites is that they can not be oxidized by oxygen but in the presence of nitrous oxide they exhibit a redox transition property Fe(II) ↔ Fe (III) [Panov *et al.*, 1998] responsible for the catalytic oxidation. The binuclear Fe(II) sites generated by the autoreaction of Fe(III) can reversibly interact with N_2O, generating so-called "*α*-oxygen" species [Yuranov *et al.*, 2004]. This oxygen radical was proved to be an anion radical O^- and the reaction was assumed to proceed through the stoichiometric deposition of one oxygen atom per each active Fe(II) atom [Panov *et al.*, 2006]. However, the structure and role in the catalysis by the Fe(II)-containing species are still unclear. Different species may be responsible for the catalyst activity in different reaction conditions. Using Fe-based zeolite catalyst, the selectivity for phenol was achieved up to 99% at phenol yield of up to 40 % [Motz *et al*., 1997].

In many studies of the selective oxidation of benzene by nitrous oxide over zeolite catalyst found that the catalyst activity gradually decreased with the increase of rection time due to catalyst deactivation by coke [Kharitonov *et al*., 1993; Motz *et al*., 1998; Häfele *et al*., 1997; Burch and Howitt, 1993; Ivanov *et al*., 2003]. The mechanisms of coke formation were studied by many researchers and the conclusions were reported differently. Burch and Howitt in 1993 purposed that the deactivation of catalyst is due to the carbonaceous deposition blocking the zeolite structure. Ivanov *et al*. in 2003 claimed that the deactivating effect of coke is caused by poisoning of active sites of catalyst. In 2002, Reitzmann *et al*. studied the kinetics of benzene oxidation with nitrous oxide and pointed out that the coke formation was caused by further oxidation, dehydrogenation and oligomerisation of phenol formed in the active sites of catalyst. The study of Zhai *et al*. in 2005 showed that the coking processes caused by organic compounds and the Brønsted acid sites are the active sites of the coke formation similarly to other coke formation over zeolite catalyst. The main components of coke consist of aromatic with alkyl and multiring hydrocarbon. Moreover, it can also consist of some aromatic with hydroxyl groups which may be caused by further oxidation, dehydrogenation and polymerization of phenol formed on Lewis acid sites. In 2003, Ivanov *et al*. reported that the zeolite catalysts can be regenerated in both oxygen and nitrous oxide, however, nitrous oxide was found to be more efficient. In the case of zeolite regeneration in nitrous oxide, a complete restoration of catalytic activity requires the removal of only 30–35% coke. In the case of regeneration in oxygen, this requires the removal of 60–65% of total coke amount.

Solutia Corp. (formerly the chemical division of Monsanto) and the Boreskov Institute of Catalysis (Russia) have developed a new technology, AlphOx, to produce phenol from the oxidation of benzene using nitrous oxide. The pilot plant has been operated since 1996 and provided benzene conversion up to 30% with phenol selectivity more than 95% using ZSM-5 catalyst. The first commercial plant is scheduled to start up by 2000 at Solutia’s Pensacola. The economic advantage comes from the free nitrous oxide available as gas-off stream from their adipic acid production at Solutia’s Pensacola. The economic evaluation of a plant using the gas-off stream indicates that the total fixed capital investment for AlphOx is lower than the conventional cumene-based phenol process. Moreover, the net production cost for AlphOx is also competitive and is not affected by fluctuations in the acetone market. However, the phenol plant capacity is limited by the availability of N_2O recovered from the adipic acid process. A relatively small phenol plant requires a world-scale adipic acid plant for its N_2O supply in which may not be economical with the conventional cumene-based process. A commercial large-scale, on-purpose generation of N_2O would solve the limitation problem of the AlphOx plant.

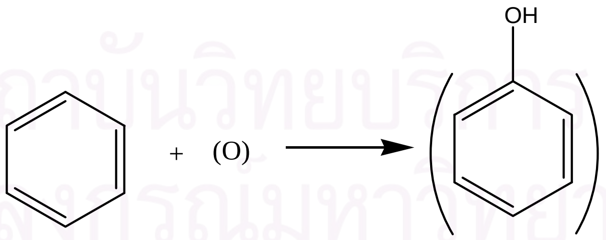
2.4.2 Oxidation with in-situ produced nitrous oxide

For the oxidation of benzene using nitrous oxide, the economic of other producers who are not in the adipic acid manufacturing depends on the ability to produced or purchase nitrous oxide at the low price. Due to this fact, the approach to produce nitrous oxide is via catalytic oxidation of ammonia using oxygen as shown below;

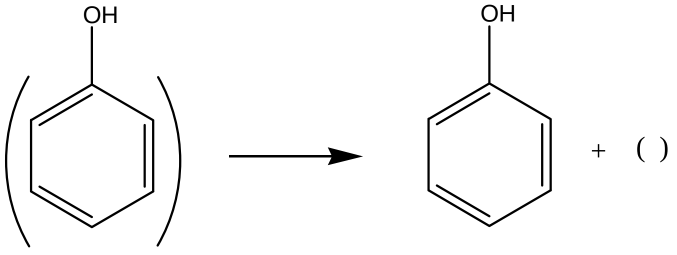
$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O \qquad \textbf{(2.2)}$$

In the next step, the formation of reactive oxygen species is produced from in-situ N_2O over the active center of suitable catalyst [Liptáková *et al.*, 2000] as follows;

$$N_2O + (\;) \rightarrow (O) + N_2 \qquad \textbf{(2.3)}$$



(2.4)



(2.5)

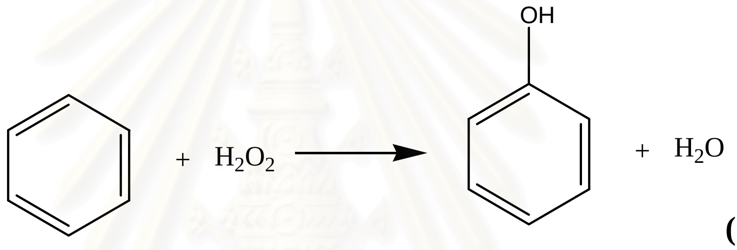
In 2004, Bahidsky and Hronec studied the reaction of benzene to phenol over various phosphates catalysts and found that phosphate catalysts containing one metal atom from the IIA group and one transient metal in the structure gave a promising catalytic effect. Nitrous oxide is formed in situ in the presence of air and ammonia. Benzene is then converted to phenol with high selectivity. Copper modified calcium phosphate, was found to be the most active catalysts among phosphates containing other metals (Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Zr, Mo, Ag, Ba, Hg). Cu-Ca-phosphate containing 47% Cu gave the highest yield, 1.3%, with 96% phenol selectivity.

Mixed hydroxyapatite catalysts containing transition metal were also reported as the catalyst for direct oxidation of benzene to phenol with in-situ produced nitrous oxide from ammonia and oxygen [Bahidsky and Hronec, 2004; Liptáková *et al*., 2000]. The mixture of oxygen-ammonia-water vapor was introduced to the system at 350°C to 450°C under atmospheric pressure. The consecutive reaction of phenol with ammonia produced aniline in a less amount and others products were biphenyl, diphenyl ether, benzofuran, dibenzofuran and benzo-1,4-dioxime. Among the hydroxyapatite containing transition metal catalyst, the Cu and Ca bimetallic hydroxyapatite gave the highest activity with almost 97% selectivity to phenol and benzene conversion was achieved at about 3-4% [Liptáková *et al*., 2000]. Nitrous oxide was formed in the first step via the oxidation of ammonia and then decomposed to active oxygen species on the active site and then directly attached to benzene to form phenol [Liptáková *et al*., 2000]. The presence of water helped to strip phenol product from the catalyst preventing the decomposition or oxidation of phenol as well as preventing the structure destruction of the hydroxyapatite catalyst under high ammonia concentration condition [Liptáková *et al*., 2004]. Another pathway of phenol production under air-ammonia aqueous system purposed by Bahidsky *et al*. in 2004 is that over modified calcium phosphate catalysts, phenyl radical is formed and further reacts with water, producing phenol and reducing Cu^+ and H^+ ions on the catalyst. These reduced forms can be re-oxidized by oxygen or nitrous oxide which is in-situ produced from the oxidation of ammonia.

In 1994, Mitsui started up a 450 metric ton per year nitrous oxide plant in Osaka, Japan. A new technology to produce nitrous oxide via catalytic oxidation of ammonia with oxygen is used in this plant. In the Mitsui technology, oxygen is used as the oxidant instead of air in order to minimize the difficulties in separating the nitrous oxide from nitrogen. However, the nitrogen free product is purposed to use for anaesthetic. In the case of oxidizing benzene to phenol, the use of air is more preferable and nitrogen is already present as a byproduct from the benzene oxidation.

2.4.3 The selective oxidation of benzene using hydrogen peroxide

The selective oxidation of benzene using H_2O_2 as an oxidant is one alternative for phenol production. The reaction of benzene and H_2O_2 produces water as the by-product which is attempted as a green process proceeding under mild conditions as shown below;



(2.6)

For industrial processes, heterogeneous catalysts have more advantages over homogeneous catalysts such as catalyst recovery and recycling. In the heterogeneous system, numerous studies are reported on the hydroxylation of benzene over various catalysts using different co-solvents in order to homogenize the mixture of benzene and H_2O_2. Phenol is usually found as the main observed product. Hydroquinone, catechol and 1,4-benzoquinone have been observed as the consecutive products form from the further oxidation of phenol. The catalyst containing titanium and vanadium species were reported with a remarkable catalytic activity. For vanadium containing catalyst, Das *et al*. in 1995 reported the used of polymer supported vanadyl (VO^{2+}) as the catalyst in the selective oxidation of benzene using acetronitrile as solvent at 65°C. During the reaction, VO^{2+} species were oxidized by H_2O_2 to form V^{5+} oxo-peroxo species which were active for the reaction. The best result was observed at 30% benzene conversion with 100% phenol selectivity without leaching of the metal. Vanadium-substituted heteropolymolybdates were synthesized and tested by Zhang *et al*. in 2005. Various solvents namely formyl acid, glacial acetic acid, propyl acid, butyric acid and acetonitrile were tested and the best result was found by using glacial acetic acid. Different vanadium species such as $NaVO_3$, $H_4PMo_{11}VO_{40}$, $H_5PMo_{10}V_2O_{40}$ and $H_6PMo_9V_3O_{40}$, are found to be catalytically active for the selective oxidation of benzene with satisfactory results, 91% phenol selectivity and yield of 26%. One of the studies for supported vanadium oxide catalyst has done by Lemke *et al*. in 2003. The vanadium catalysts were prepared using various support materials such as MCM-41, MCM-48, SiO_2 and amorphous microporous mixed oxide (AMM). The best result was obtained at 8.3% phenol yield over VO_x/SiO_2 catalyst with low % vanadium loading (0.14 wt.%) using acetic acid as co-solvent. In 1999, Chen and Lu have proved that V/MCM-41 prepared with hydrothermal synthesis was more active than that prepared with impregnation. Benzene conversion up to 18% was reported with maximum phenol selectivity around 40%.

Clay supported vanadium oxide was studied by Gao and Xu in 2006, using acetic acid as solvent. The physical mixture of clay and V_2O_5 catalyst exhibited lower activity than V_2O_5/clay prepared by impregnation method. The changes in peak position of the V=O stretching mode in FT-IR spectra for vanadium impregnated on clay attributed to the interaction between vanadium and clay, was believed to be a role to promote the selective oxidation of benzene to phenol. Under mild reaction condition such as 40°C, high selectivity to phenol of 94% with 14% benzene conversion was achieved using the optimum 2.5% vanadium loading. The excessive of vanadium oxide decompose H_2O_2 resulted in low conversion. In 2003, Remias *et al*. studied the amount of vanadium loading on the activity for this reaction and found the optimum critical vanadium loading. It was interpreted by the assumption that the active species of vanadium in the selective oxidation of benzene to phenol was monomeric vanadium species. The excess of vanadium loading favored the existence of vanadium in the form of inactive m-oxo dimmer.

For titanium containing catalyst, Ti-substituted into framework of zeolite was used in many organic transformation especially TS-1 which has been the subject for many studies in the selective oxidation reaction using H_2O_2. In the selective oxidation of benzene, preparation methods, the existence of extra-framework titanium, traces of sodium, the reaction condition and the present of co-solvent in the mixture have an influence on the catalytic activity. In 1990, Thangaraj *et al*. studied the selective oxidation of benzene with H_2O_2 over various catalysts in zeolite family. They found that benzene remained unreacted over silicalite-1, TiO_2 (both amorphous and crystalline), and also in the absence of catalysts. The selectivity for the conversion of H_2O_2 to oxygenated products 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), 1,4-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 1,4-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. Bianchi *et al*. in 2007 and Balducci *et al*. in 2003 investigated the selectivity oxidation of benzene using different solvents namely acetone, acetonitrile, methanol, tert-butyl alcohol, acetic acid, dimethylformamide, N-methylpyrrolidone, dimethylsulfone, and sulfolane over a series of catalysts, obtained by modification of titanium silicalite (TS-1). The modification was done by simple treatment with $(NH_4)OAc$, $(NH_4)HF_2$, H_3PO_4/H_2O_2, H_2SO_4/H_2O_2, HF/H_2O_2, $(NH_4)F/H_2O_2$ and $(NH_4)HF_2/H_2O_2$ in purpose to remove the less selective catalytic sites of the catalyst. The best results were obtained after post-synthesis treatment the catalyst with $(NH_4)HF_2$ and H_2O_2. Using nitrogen containing solvents, such as dimethylformamide, promotes the unproductive decomposition of hydrogen peroxide, and N-methylpyrrolidone, that depresses the catalytic activity of TS-1 results in low conversion. Co-solvents containing sulfone group, such as dimethyl sulfone and tetramethylene (sulfolane) allowed the conversion of benzene close to 8% with the selectivity to phenol higher than 80% at 100°C. Sulfolane is a solvent with high dipole moment (4.81 Debye) and dielectric constant (43.26) showing the peculiar property to form a sterically hindered species with phenolic compound. This complex cannot enter the titanium silicalite pores, thus inhibiting the further oxidation of phenol to dioxygenated compounds. In 2001, He *et al*. have studied the hydroxylation of benzene over Ti-MCM-41 catalyst using acetone as solvent. The large pore Ti-MCM-41 offered the great advantage of benzene substrate to diffuse and react on the active site and also phenol diffuse away from the actives site. The hydrophilic property of the surface favors the hydroxylation of benzene over the oxidation of phenol and yields the selectivity of phenol close to 100%. The conversion of benzene increased when increased the titanium content and the introduction of Al. The best value of conversion was reported at 98% with more than 95% phenol selectivity for [Si, Ti, Al]-MCM-41 (Si/Ti = 25 and Si/Al = $\propto$) much better TS-1 catalyst which gave 10% benzene conversion and 63% phenol selectivity. The reduction in activity was observed when reused the catalyst but it can be regenerated by calcinations. In 1994, Tanev *et al*. reported 68% conversion and 98% phenol selectivity in the same reaction system using Ti-MCM-41 (Si/Ti=100) as the catalyst.

Only few studies reported the reaction under the most preferable, solvent-free system. In 2003, Lemke *et al*. studied vanadium-containing catalysts based on MCM-41, MCM-48, silica (Aerosil) and AMM (metal content 0.1–2.5 wt.%) in the selective oxidation of benzene under “triphase” system at room temperature to 100°C, Unfortunately, the observed benzene conversion was very small (<2%) with phenol selectivity up to 97% at 70°C. Better results were reported by Lin *et al*. over silylated Ti-MCM-41 catalyst in 2005. The silylation of Ti-MCM-41 surface by trimethylchlorosilane in the vapor phase was applied in order to improve the hydrophobicity through the formation of surface groups of $(CH_3)_3SiOSi(OSi)_3$ during silylation. 29Si MAS NMR spectra of the catalyst after the silylation process of 5-9 h exhibited new titanium species, $(CH_3)_3SiOTi(OSi)_3$ which should response for the better catalytic activity than conventional titanium species in Ti-MCM-41. The best result of benzene conversion was observed around 18.7% with 92.6% phenol selectivity over Ti-MCM-41 silylated for 9 h.

The remarkable results in solvent free system have been obtained by using TS-1 as catalyst. This kind of catalyst is commercialized for the production of hydroquinone and catechol by hydroxylation of phenol [Yokoi *et al*., 2003]. In solvent-free system, Kumar and Bhaumik in 1999 and Bhaumik *et al*. in 1998 have reported the significant enchantment of reaction rate of benzene hydroxylation compared with bi-phase system. The increase 4-6 times activity when the reaction is performed in triphase instead of biphase was found. This is due to the presence of solvent caused a diffusion hindrance of benzene molecule inside the TS-1 channel and such hindrance is not encounter in solvent-free system. The maximum conversion was reported around 78% benzene conversion and 86% phenol selectivity at 70°C using benzene/H_2O_2 molar ratio of 1:1 [Bhaumik *et al.*, 1998]. Kamar and Bhaumik in 1999 reported the increase of benzene conversion from 10.9% to 78.5% and the increase of phenol selectivity from 85% to 89% when water was used instead of acetronitrile. However, the repeated study under solvent-free conditions by Bianchi *et al.* in 2007 was sensibly lower than that reported by Bhaumik *et al.* in 1998. The benzene conversion was observed only at 4.5% with 42% phenol selectivity under the identical conditions.

Another study in triphase system over TS-1 catalyst was done by Bengoa *et al.* in 1998. Around 17% conversion based on H_2O_2 with 74% phenol selectivity was reported under their conditions. The decease in activity was observed when methanol was used instead of water. The study using UV-Vis technique proved the competitive absorption of methanol that it can compete with H_2O_2 to adsorb on TS-1 catalyst but this competitive adsorption does not totally prevent the H_2O_2 adsorption.

2.4.4 Oxidation with molecular oxygen

Due to the cost of hydrogen peroxide is high and the use of nitrous oxide has economic advantage only when nitrous oxide comes from by-product of adipic acid production. One possibility to produce phenol in one-step with the lowest cost of oxidizing reagent is the oxidation using molecular oxygen. The gas phase oxidation of benzene to phenol requires high temperature resulting in a significant oxidation of benzene to carbon oxide and low phenol selectivity is usually obtained. In 2005, Bahidsky and Hronec studied the oxidation of benzene over O_2-H_2O system at 450°C using Cu–Ca–phosphate catalyst and found that, the main product was CO_2 with 7.1% yield and only 3.2 % phenol yield was achieved. In general, decreasing the reaction temperature tends to improve phenol selectivity. At 180-240°C using V-containing oxides catalyst, the selectivity of phenol reached 90% [Durante *et al.*, 1999]. Nevertheless, lowering the temperature leads to the lower productivity down to several gram of phenol per kg of catalyst per hour as well as the deactivation of catalyst from a reduction of the oxides [Kuznetsova *et al.*, 2005].

The challenge of using oxygen is to activate it with the aid of reducing agent. Oxygen in the form of activated oxygen thus could be attained in the selective oxidation of benzene to phenol under mild condition. Oxygen gas can be activated into a neutral oxygen species by mixing with a proper reductant, such as carbon oxide, ascorbic acid or hydrogen. In gas phase reaction, Cu^{2+} ion-exchanged Y-type zeolites have been indicated to have redox properties according to physico-chemical measurements. Therefore, Yamanaka *et al*. in 2002 have reported the oxidation of benzene to phenol over various Cu supported oxides catalyst using molecular oxygen in the present of carbon monoxide. Among the various supports including SiO_2, $SiO_2.Al_2O_3$, Al_2O_3, NaY, HY, NaX, HX, NaM, KL, NaZSM-5 and HZSM-5, the results showed only Cu-ZSM-5 systems were found to have catalytic activity. The best result obtained from Cu ion-exchanged with HZSM-5 (0.93 wt.% Cu) was around 1.5 % phenol yield at 400°C but the deactivation was observed resulting in decreasing of phenol yield with time. The further study on Cu-ZSM-5 catalyst system has been reported by Castagnola *et al*. in 2005. The catalysts with different amount of Cu and Si/Al have been synthesized and studied the nature of catalyst using X-ray absorption spectroscopy. The study have suggested that Cu which existed as the isolated ions were the active sites for phenol formation. The doping of silver and palladium increased the activity but the selectivity to phenol remained the same. The conversion after 20 h time on steam was reported at 3 % with 47% phenol selectivity over PdAgCu-ZSM-5 catalyst. It was suggested that the presence of water increased the selectivity of phenol by displacement product from active site and preventing deep oxidation of product.

The use of oxygen as an oxidant has been carried of in the presence of H_2 over the catalyst system consisting of Pt, Pd, Rh, Ir and transition metal oxides. Hydrogen peroxide is formed in situ from a mixture of O_2 and H_2 in the presence of the catalyst and subsequently decomposed to hydroxyl radicals. In 1995, Miyake *et al*. reported the oxidation of benzene using O_2 using the precious metal supported on silica system. The order of the rate of phenol formation was $Pt/SiO_2 > Rh/SiO_2 > Ir/SiO_2 > Pd/SiO_2 > Ru/SiO_2$. All the catalysts modified with vanadium oxide gave higher rates of phenol formation compared to the catalysts without modification. Kitano *et al*. in 1994 observed benzene conversion around 0.9% using Pd-Cu/SiO_2 at 200°C.

Similarly, Pt/VO_x/SiO_2 or Pd/VO_x/SiO_2 catalyst system exhibited around 0.68-0.97% benzene conversion at the temperature 150-200°C [Ehrich *et al.*, 2002]. The yield of phenol, however, has been inadequate for practical use. Moreover, using of H_2/O_2 mixture in a large-scale synthesis is not preferred. The reaction condition is restricted by the explosion limit of the H_2/O_2 mixture.

To avoid the risk of explosion, many studies have been done in liquid phase using acetic acid or hydrochloric as solvent. Precious metal mixed with metal oxide such as Pd–Cu/SiO_2 [Kunai *et al.*, 1990], Pd, Pt–V_2O_5/SiO_2 [Hamada *et al.*, 1993], Pt, Rh, Ir, Pd or Ru supported on SiO_2 modified with V_2O_5, Y_2O_3, Nb_2O_5,WO_3, La_2O_3 or MoO_3 [Miyake *et al.*, 1995], Pd/Ti-silicalite [Tatsumi, 1993] have been used. The results exhibited benzene conversion in the range 0.1-0.6% with over 90% phenol selectivity. The requirement of acid solvent and low productivity brings about the unattractive of this system.

In 2004, Kanzaki *et al*. have reported the liquid-phase oxidation of benzene to phenol catalyzed by Cu catalysts supported on various oxides including SiO_2, TiO_2, Al_2O_3 , SiO_2-Al_2O_3 and MCM-41 using gaseous oxygen, ascorbic acid and acetic acid as a oxidant, reducing reagent and solvent, respectively. The yield of phenol was obtained in the range 0.6-2.5%. In addition, Cu leaching at acetic acid concentrations of more than around 40–60 vol.% was observed. Vanadium catalysts supported on SiO_2 and Al_2O_3 have also been studied for the gaseous O_2/reducing agent/acetic acid system [Masumoto *et al.*, 2004]. Ascorbic acid, hydroquinone, pyrocatechol, oxalic acid, *i*-Butyl aldehyde, sodium sulfite and zinc acetate have been used as the reducing agent but the good result was found only when ascorbic acid was used. Phenol yield was reported to increase with the increase in the concentration of acetic acid in the aqueous solvent, and had a maximum value around 8.6% at the acetic acid concentration of around 80 vol.%. Under those conditions, vanadium leaching was observed around 61%.

2.4.5 The selective oxidation of benzene in the H_2/O_2 reductive membrane system

The direct oxidation of benzene using oxygen and hydrogen is dangerous and relatively difficult reaction. Using a membrane reactor is an alternative way to avoid explosions and successfully control the process, in which oxygen and hydrogen can be supplied separately. Another problem for the oxidation reaction with molecular oxygen is the destruction of aromatic ring resulting in low phenol selectivity. The challenge of using oxygen as the oxidant would be how to produce active oxygen species from the molecular oxygen attack to benzene and reduce the further oxidation of organic compound. Membrane reactor seem to be the effective method which can allow H_2 atom dissociate on the surface and diffuse through the membrane to react with oxygen in other side to produced active oxygen species. In 2003, Itoh *et al*. have suggested that active hydrogen permeating through palladium membrane activated the oxygen to form active species like O or OH radicals. Benzene is expected to be attacked by these radicals and hydroxylated. The oxidation in this system takes place only on the membrane surface. Therefore, the product will have less chance to be further oxidized resulting in high product selectivity.

Figure 2.8 Concept illustration of the selective oxidation of benzene to phenol using Pd membrane reactor [Sato *et al*., 2005].

The optimum ratio of H_2/O_2 feed gave the conversion around 25-30% with 77% phenol selectivity at 200°C. Other observed products were cyclohexanone, cyclohexene, cyclohexane oxide, cyclohexane and 1,4-cyclohexadiene [Itoh *et al*., 2003]. In 2005, Sato *et al*. reported 15% benzene conversion with phenol selectivity of 95% using Pd membrane coated on a porous α-Al_2O_3 tube at the operation temperature of 150°C.

2.5 Comment on previous works

From the previous studies of the selective oxidation of benzene to phenol in one step, it can be seen that various oxidants such as nitrous oxide, molecular oxygen or molecular oxygen with reducing agent such as H_2, CO and ascorbic acid, the mixture of oxygen/ammonium and hydrogen peroxide were investigated. Using nitrous oxide as oxidant has economic advantage only when nitrous oxide is an off-gas from the adipic acid production and it is clean. The commercial plant is scheduled to start up by 2000 at Solutia's Pensacola. Unfortunately, in 2001, Solutia announced a mutual agreement with JLM Industries, Inc. (Nasdaq: JLMI) to end the commercial agreement for establishing a new benzene to phenol plant due to imbalance in supply/demand for phenol during that period. The use of molecular oxygen or air as oxidant, oxygen/hydrogen system and oxygen/ammonium system result in low conversion and quite often in low selectivity. Hydrogen peroxide seems to be an attractive oxidant, which can be applied in a green process under mild conditions. The results of the previous work showed a very high conversion and selectivity over TS-1 [Bhaumik *et al.*, 1998] and Ti-MCM-41 [He *et al*., 2001]. Nevertheless, there is still no commercial plant based on that process even though those findings have been published for almost 10 year. The ability to obtain such high benzene conversion with excellent phenol selectivity is still in the subject of controversy among the phenol producers. The newest phenol plant built by PTT groups, Thailand, still use the conventional process based on cumene route (UOP technology) with the production capacity of 200,000 tons per year of phenol and 125,000 tons per year of acetone.

Therefore, it was of great of interest to improve the most preferable, solvent-free system using H_2O_2 as the oxidant over the new catalyst which has special properties to convert benzene to phenol selectively.

CHAPTER III

EXPERIMENTAL

This chapter consists of experimental systems and procedures used in this study. The chapter is divided into five sections. The procedures of TS-1 and Ti-MCM-41 catalyst preparations are explained in section 3.1. The composition, structure and surface properties of the catalyst characterized by various techniques such as ICP-AES, XRD, N_2 adsorption-desorption isotherm, FT-IR, DRUV-Vis and SEM are explained in section 3.2. The details of the catalytic reaction procedures and H_2O_2 decomposition study are illustrated in section 3.3 and 3.4, respectively. Finally, the calculations of conversion and product selectivity are described in section 3.5.

Scope of the study

The reaction conditions are chosen as follows:

Catalyst	:	Titanium-Silica based catalyst such as TS-PQ^{TM}, TS-1 and Ti-MCM-41 catalyst
Reactant	:	Benzene (in liquid phase)
Oxidant	:	30 wt. % hydrogen peroxide aqueous solution
Type of reactor	:	Round bottom flask and autoclave
Reaction pressure	:	Atmospheric pressure and 20 bar of N_2
Reaction temperature	:	60°C to 75°C
Stirring speed	:	500 rpm to 1100 rpm
Benzene/H_2O_2 molar ratio	:	1:1, 3:1, 5:1, 7:1 and 10:1
Additional water	:	Up to 60 ml
Catalyst weight	:	0.2 g to 2.5 g
Reaction time	:	0.5 h to 5 h

3.1 Catalyst preparation

3.1.1 Preparation of TS-1 catalyst

TS-1 catalyst was prepared by hydrothermal method according to the procedure of Bhaumik *et al.* in 1998. The chemicals used in the preparation procedure of TS-1 are shown in **Table 3.1**.

Table 3.1 The chemicals used in the preparation of TS-1 catalyst.

Chemical	Supplier
Tetraethyl orthosilicate (TEOS)	Fluka
Tetrapropyl ammoniumhydroxide, 20 wt.% (TPAOH)	Fluka
Tetra-*n*-butyl titanate (TNBT)	Fluka
Isopropyl alcohol (IPA)	Aldrich
Hydro phosphoric acid, 85% aq. (H_3PO_4)	Riedel de Haen
Sulfuric acid (H_2SO_4)	Merck

The solution mixture of silica, titanium and template solvent was prepared at the molar composition of 1.0 TEOS : 0.033 TNBT : 0.4 TPAOH: 0.75 IPA : 0.067 H_3PO_4 : 25.0 H_2O. The silicate solution was prepared by adding TEOS in an amount of 42 g to 81.2 g of TPAOH solution under vigorous stirring. The mixing was performed continuously for 1 h. After that, the mixture of 2.24 g TNBT in 9 g isopropyl alcohol was added slowly into the clear silicate solution. H_3PO_4 1.54 g was dissolved in 9 g of water and added again to the silicate solution. The stirring was continued for another 1 h. The obtained clear solution was autoclaved at 160°C for 6 h. After crystallization, the solid was separated, washed thoroughly with deionized water, dried over night and calcined at 500°C for 16 h. The calcined sample was treated with dilute H_2SO_4 solution (3 wt.% aqueous solution) at room temperature for 2 h and then centrifuged, washed thoroughly with deionized water and dried.

3.1.2 Preparation of Ti-MCM-41 catalyst

Ti-MCM-41 catalyst was prepared by hydrothermal method using a home made $(NH_4)_3[Ti(O_2)F_5]$ as the titanium source [Nießen *et al.*, 1998]. The chemicals used for Ti-MCM-41 preparation are listed in **Table 3.2**.

Table 3.2 The chemicals used in the preparation of Ti-MCM-41 catalyst.

Chemical	Supplier
Titanium dioxide (TiO_2)	Hombikat
Hydrofluoric acid (HF)	Fluka
Hydrogen peroxide, 30 wt% aq. Solution (H_2O_2)	Merck
Ammonium aqueous solution	Merck
Ethanol	Aldrich
Tetradecyltrimethyl ammonium bromide	Fluka
Tetraethyl ammonium hydroxide, 40% aq.	Fluka
Silica aerosil	-

3.1.2.1 The synthesis of titanium source $(NH_4)_3[Ti(O_2)F_5]$

In the first step, 2 g of TiO_2 (25 mmol TiO_2) was dissolved in 21 g of 40 wt.% HF aqueous solution (420 mmol HF) in a Teflon beaker firmly hold in a water bath with heating at 70°C. After TiO_2 was totally dissolved, the beaker was cooled down to 20°C and then 0°C (ice bath). At 0°C, 19.992 g of 30 wt.% H_2O_2 aqueous solution (176.4 mmol H_2O_2) was added slowly and the solution was stirred for 10 min. Afterwards, the small portions of 25 wt.% NH_3 aqueous solution were added with stirring to adjust the pH of the mixture until the pH of the solution was 6. The product was separated by filtration, washed three times with ethanol and dried with vacuum under concentrated sulfuric acid. A dark yellow powder product is obtained after the final step.

3.1.2.2 The synthesis of Ti-MCM-41

Ti-substituted MCM-41 was synthesized using tetradecyltrimethyl ammoniumbromide and tetraethylammoniumhydroxide (40 wt.% TEAOH aqueous solution) as template, silica aerosil as the silica source and the home made $(NH_4)_3[Ti(O_2)F_5]$ as the titanium source. In the first step, 2.7 g of silica aerosil and 142.11 g of water were mixed in a Teflon vessel. Then, 16.65 g of tetradecyltrimethyl ammoniumbromide were added following by the addition of 25.68 g 40 wt.% TEAOH under vigorous stirring. Afterward, 0.81 g of $(NH_4)_3[Ti(O_2)F_5]$ were added under stirring for 1 hour at room temperature. Finally, 11.75 g of silica aerosil were added and the stirring was continued for another 5 hours. The product was crystallized at 100°C for 7 days. After crystallization, the solid was separated, washed thoroughly with deionized water and dried over night. The product was calcined at 550°C for 10 hours.

3.2 Catalyst characterization

3.2.1 Determination of catalyst composition

The composition analysis of elements in the bulk of the catalyst was performed by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) with a spectroflame D (Spectro Analytic Instrument).

3.2.2 X-ray diffraction (XRD)

The crystallinity and X-ray diffraction patterns of the catalysts were performed on SIEMENS D5000, using Nickel filtrated Cu Kα radiation. The operating conditions of the instrument are shown below:

2θ range of detection:	1.5^{o} to 40^{o}
Scanning period	0.02 °/min

3.2.3 N_2 adsorption-desorption isotherm

Nitrogen adsorption isotherms were obtained at -196°C on Micromeritics ASAP 2010 Gas Sorption and Porosimetry System. Approximately 0.3 g of powder samples were dehydrated under vacuum for 3 h before the measurement. The adsorption-desorption was conducted by passing nitrogen through the sample cell which was immerged into liquid nitrogen. Brunauer-Emmett-Teller (BET) surface areas were determined under the relative pressure range between 0.05 and 0.20. Micropore area, micropore volume and average pore diameter were calculated from the adsorption branch of the isotherms using Barrett-Joyner-Halenda (BJH) method. From the adsorption-desorption data, Horvath-Kawazoe model was chosen to calculate average pore diameter of microporous materials.

3.2.4 Fourier Transform Infrared (FT-IR)

The functional group on the catalyst surface was determined by FT-IR using Nicolet Protégé 460. Each sample was mixed with KBr with ratio of sample: KBr equal to 1:100. The powder was crushed and then pressed into a thin wafer. Infrared spectra were recorded between 400 cm^{-1} and 4000 cm^{-1} on a microcomputer. The ratio of the intensity between 960 cm^{-1} and 800 cm^{-1} band was calculated with the help of ORIGIN® program

3.2.5 Diffuse reflectant UV-Vis spectroscopy (DRUV-Vis)

Diffuse-Reflectance UV-Vis spectra were recorded on Perkin Elmer Lambda 950 equipped with diffuse reflectance attachment with $BaSO_4$ as the reference.

3.2.6 Scanning electron micrographs (SEM)

Scanning electron micrographs (SEM) of TS-PQ™ catalyst was provided by PQ Corporation. SEM picture of TS-1 and Ti-MCM-41 catalysts were taken using S-3000 N Hitachi.

3.3 Catalytic reaction

3.3.1 Chemicals

The chemicals used in the studied reaction are shown in **Table 3.3**.

Table 3.3 The chemicals used in the studied reaction.

Chemical	Supplier
Benzene	Panreac
Hydrogen peroxide (30 wt.% aqueous solution)	Fisher
Methanol	Aldrich
tert-Butylalcohol	Aldrich
Acetronitrile	Aldrich
Acetone	Aldrich
Ethanol	Aldrich

3.3.2 Apparatus

The catalytic tests were performed in batch systems. Two types of reactor, round bottom flask glass reactor and autoclave, were used. The equipments used in this system are explained as followed:

3.3.2.1 Round bottom flask reactor system

A round bottom flask with three necks was used as the reactor under atmospheric pressure. One neck was connected to a condenser cooling with cold water and another two necks were connected to the injection port and a thermometer, respectively. A hotplate-magnetic stirrer with variable speed and an oil bath were used for heating and stirring the mixture. A plastic syringe connected with a needle was used for adding the substrates to the reactor. The experimental setup for round bottom flask reactor is shown in **Figure 3.1**.

Figure 3.1 The experimental setup for round bottom flask reactor.

3.3.2.2 Autoclave

The autoclave is made from stainless steel enveloped with an electric heating jacket, controlling the temperature by using a thermocouple and Eurotherm 91e temperature controller. The maximum temperature and pressure for safety operation is 300°C and 100 bar. 25 ml glass holder was placed inside and used as a mixture container. Magnetic stirrer with variable stirring speed was used for stirring the reaction mixture. The experimental setup for autoclave system is shown in **Figure 3.2**.

Figure 3.2 The experimental setup for autoclave system.

3.3.2.3 Mini-centrifuge

The catalyst particle was separated after the reaction by using mini-centrifuge equipped with six tube rotors (1.5 ml tube size).

3.3.2.4 Gas chromatograph

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

Table 3.4 Operating conditions for gas chromatograph (Shimadzu GC9A).

Gas chromatography	Shimadzu GC9A
Detector	FID
Packed column	GP 10% SP-2100
Carrier gas	N_2
Carrier gas flow rate	30 ml/min
Injector temperature	250^{o}C
Detector temperature	250^{o}C
Initial column temperature	70 ^{o}C (5 min isotherm)
Program rate	6^{o}C/min
Final column temperature	160^{o}C
Analyzed chemicals	Phenol, Catechol, Hydroquinone and 1,4-Benzoquinone

Under the GC conditions above, the retention time of products are listed in **Table 3.5.** The preparation of standard sample and the calibration curve for product analysis are described in **Appendix A**.

Table 3.5 The retention time of products for gas chromatograph Shimadzu GC9A.

Product	**Retention time (min)**
1,4-Benzoquinone	10
Phenol	12
Catechol	19
Hydroquinone	23

For the experiments carried out at the Institute of Chemical Technology and Heterogeneous Catalysis, RWTH-Aachen University in Germany. The samples were analyzed using a gas chromatograph HP 6890 equipped with a FID detector and capillary column. The GC conditions are listed in **Table 3.6**. The retention times of interested products are list in **Table 3.7**.

Table 3.6 Operating conditions for gas chromatograph (HP 6890 Plus).

Gas chromatography	**HP 6890 Plus**
Detector	FID
Capillary column	CP-SIL8; 60 m length
Carrier gas	N_2
Carrier gas flow rate	13.2 ml/min (Split ratio 8.2:1)
Injector temperature	250^{o}C
Detector temperature	280^{o}C
Initial column temperature	50^{o}C (6 min isotherm)
Program rate	10^{o}C/min
Final column temperature	270 ^{o}C (20 min isotherm)
Analyzed chemicals	Phenol, Catechol, Hydroquinone and 1,4-Benzoquinone

Table 3.7 The retention time of products for gas chromatograph HP 6890.

Product	**Retention time (min)**
1,4-Benzoquinone	12
Phenol	14
Catechol	18
Hydroquinone	20

3.3.3 Reaction procedure

The procedure steps for the selective oxidation of benzene carried out in round bottom flask reactor under various reaction conditions are described in the detail below.

1. The catalyst was dried at 110°C to remove water before weighting into the reactor.

2. Additional water, apart from that obtained through H_2O_2 solution, was normally used at 20 ml, unless stated otherwise. Magnetic stirring bar was added before placing the reactor into the oil bath. The reactor was connected to the condenser, injection port and thermometer. Circulated cold water was pumped to the condenser.

3. The reactor was heated up to the reaction temperature. After reaching the desired temperature, liquid benzene was injected, thereby avoiding benzene evaporation during the heating up process.

4. The reaction was started by slowly adding drop-wise of 30 wt.% hydrogen peroxide aqueous solution to the mixture with the help of an appropriate syringe.

5. After the reaction was finished, the mixture was immediately cooled down in an ice bath. Ethanol or methanol was used to homogenize the mixture. The required amount of solvent for homogenizing the mixture of benzene-water was calculated by

using triangular curve for three phase system. The details of calculation are explained in **Appendix C**.

6. The catalyst particle was separated from the homogeneous mixture by using the micro-centrifuge. The peroxide test paper was then immersed to the sample for preliminary detection of H_2O_2. In the case that H_2O_2 is present in reaction mixture, manganese (IV) oxide was added to the sample to decompose H_2O_2 before injecting the sample to GC.

For the experiments studied in the autoclave, the catalyst, substrates and magnetic bar were added into 25 ml glass holder. The glass holder was placed into autoclave and closed autoclave. The heating jacket and thermocouple available from controller were connected to autoclave. The reaction was started by switching on the stirring when the temperature inside the autoclave reached the desired temperature. The sample preparation for GC analysis was done in the same way as the reaction carried out in the round bottom flask reactor.

The influence of various reaction parameters affected the performance of titanium-silica based catalyst in the selective oxidation of benzene were investigated in following:

- Methanol, ethanol, *tert*-Butylalcohol, acetone and acetronitrile were used as co-solvent in the preliminary study of TS-PQ^{TM} catalyst in the selective oxidation of benzene using H_2O_2 as the oxidant under two phase system.

- The effect of pressure was studied under 20 bar of N_2.

- The effect of H_2O_2 additional period was carried out in the range between 10 to 70 min from the starting point of the reaction.

- The effect of temperature was studied at 65°C, 70°C and 75°C.

- The effect of stirring speed was studied at 500 rpm, 900 rpm and 1100 rpm.

- The effect of molar ratio of benzene/H_2O_2 was studied by fixing the amount of H_2O_2 at 0.012 mole and varying mole of benzene from 0.012 to 0.120 mole (1:1 to 10:1 Benzene/H_2O_2 molar ratio)

- The effect of additional water volume was studied in the range of 0 ml to 60 ml.

- The effect of catalyst weight was studied by varying the catalyst amount from 0.2 g to 2.5 g.

- The effect of reaction time was studied at 0.5 h, 1 h, 2 h, 2.5 h, 3 h and 5 h.

3.4 H_2O_2 decomposition study

The method commonly used for determination of H_2O_2 concentration is the titration method. H_2O_2 is an ordinary oxidizing agent capable of accepting electrons from other substances as the reaction below;

$$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O \qquad \textbf{(3.1)}$$

However, H_2O_2 can be oxidized to form molecular oxygen by releasing 2 electrons as the equation below;

$$H_2O_2 \rightarrow O_2 + 2e^- + 2H^+ \qquad \textbf{(3.2)}$$

From the equations above, H_2O_2 can be oxidized by a stronger oxidizing agent such as permanganate ion (MnO_4^-). Under acidic condition, permanganate ion reacts with H_2O_2 to form colorless product. The first permanent pink color of permanganate ion will persist when there is no more H_2O_2 in the mixture. The reaction of H_2O_2 and permanganate is shown below;

$$5\,H_2O_2 + 3\,H_2SO_4 + 2\,KMnO_4 \rightarrow K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2 \qquad \textbf{(3.3)}$$

The permanganate titration method cannot be used when organic or inorganic matters that reduce potassium permanganate are present in the mixture. Hydrochloric acid or other chloride ions are to be avoided due to the permanganate will also oxidize chloride ions to chlorine and the titration will be subject to be errors. The presence of fluoride ions affects the permanganate titration and large proportions of calcium salts or titanic acid lead to low results.

H_2O_2 can oxidize iodide to iodine in an acidic condition. The iodine which has been produced stoichiometrically in the redox reaction may then be titrated with thiosulfate to faint yellow or straw color of iodine. This method is called iodometric titration and the reactions in the process are shown below;

$$H_2O_2 + 2KI + H_2SO_4 \rightarrow I_2 + K_2SO_4 + 2H_2O \qquad \textbf{(3.4)}$$

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6 \qquad \textbf{(3.5)}$$

The iodometry is somehow less accurate than the permanganate titration because of the oxidation of iodide by air. However, it is less susceptible to be interfered by organics.

The H_2O_2 decomposition in this study was performed separately to estimate the maximum limit of the H_2O_2 conversion to organic compounds. The decomposition of H_2O_2 in the absence and the presence of catalyst under the experimental reaction conditions were investigated. Both potassium permanganate titration and iodometric titration were applied to analyze the remaining H_2O_2 in the mixture after reaction. The procedures of the permanganate titration and iodometric titration are described below;

3.4.1 Titration with potassium permanganate

3.4.1.1 Materials

1. Demineralized or distilled water
2. Potassium permanganate (0.10 N $KMnO_4$) as titrant (may be standardized against primary standard sodium oxalate)
3. 25 vol.% sulfuric acid (pre-mixed and cooled)

3.4.1.2 Procedures

1. Measured 100 ml of distilled water into a 250 ml Erlenmeyer flask.
2. Added 10 ml of sulfuric acid solution and 1 ml to 5 ml of sample containing diluted H_2O_2 solution.
3. Titrated with potassium permanganate slowly while the solution was swirling constantly. Potassium permanganate was added dropwise when the color began to take longer time of fade.
4. Stopped adding potassium permanganate when the solution turned light purple and color persisted for 15 seconds. Read the volume of permanganate used for the titration.
5. Repeated the analysis several times and calculated the concentration of H_2O_2 according to the stoichiometry equation.

3.4.2 Iodometric titration

3.4.2.1 Materials

1. 25 vol.% sulfuric acid (pre-mixed and cooled)
2. Solid potassium iodide
3. Sodium thiosulfate (0.10 N $Na_2S_2O_3$) as a titrant (may be standardized against primary standard potassium bi-iodate solution)
4. 10 wt.% starch solution

4.4.2.2 Procedures

1. Measured 50 ml of distilled water into a 250 ml Erlenmeyer flask.

2. Added 5 ml of sulfuric acid solution and 1 ml to 5 ml of sample containing diluted H_2O_2 solution.

3. Added approximately 0.8 g of KI to the sample and swirled to dissolve the solid until the solution was well mixed.

4. Titrated with sodium thiosulfate until the brown color had been reduced to a light straw color.

5. Added a few drop of starch solution to obtain dark blue color and continued the titration until the color of the solution just disappeared. Recorded the volume of sodium thiosulfate used for the titration.

6. Repeated the analysis several times and calculated the concentration of H_2O_2 according to the stoichiometry equation.

The H_2O_2 decomposition was calculated using the equation below;

$$H_2O_2 \text{ decomposition } (\%) = \frac{n_{0.,\,H_2O_2} - n_{\text{fin..},\,H_2O_2}}{n_{0,\,H_2O_2}} \times 100 \qquad \textbf{(3.6)}$$

Where;

$n_{0,\,H_2O_2}$	is the initial mole of H_2O_2
$n_{\text{fin.},\,H_2O_2}$	is the final mole of H_2O_2 after the reaction analyzed by titration method

3.5 The calculation of conversion and product selectivity

The catalytic performance of the catalysts is evaluated in terms of H_2O_2 conversion calculated based on overall produced products. The results are related to moles of H_2O_2 because the reactant benzene can be easily separated from the three-phase system and reused. Therefore, the considerable maximum H_2O_2 utilization, however, is a desirable target. The molar H_2O_2 conversion to organic compounds, shown in equation **(3.7)** is defined as mole of hydrogen peroxide converted to oxygenated organic products including assumeably consecutive formation of 1,4-

benzoquinone, hydroquinone and catechol from phenol. One mole of phenol consumes one mole of H_2O_2 and one mole of 1,4-benzoquinone or hydroquinone or catechol consumes two moles of H_2O_2. The total H_2O_2 conversion including decomposition is calculated according to equation **(3.8)**. However, this calculation has been represented only in the study of catalyst stability.

$$C_{H_2O_2,\,Org.} = \frac{n_{Phenol} + (2 \times n_{1,4-Benzoquinone}) + (2 \times n_{Catechol}) + (2 \times n_{Hydroquinone})}{n_{0,\,H_2O_2}} \times 100 \quad \textbf{(3.7)}$$

$$C_{H_2O_2} = \frac{n_{0,\,H_2O_2} - n_{fin.,\,H_2O_2}}{n_{0,\,H_2O_2}} \times 100 \quad \textbf{(3.8)}$$

Where;

$C_{H_2O_2,\,Org.}$	is the H_2O_2 conversion to organic compounds (%)
$C_{H_2O_2}$	is the total H_2O_2 conversion (%)
n_{Phenol}	is mole of phenol after reaction
$n_{1,4-Benzoquinone}$	is mole of 1,4-benzoquinone after reaction
$n_{Catecol}$	is mole of catechol after reaction
$n_{Hydroquinone}$	is mole of hydroquinone after reaction
$n_{0,\,H_2O_2}$	is initial mole of hydrogen peroxide
$n_{fin.,\,H_2O_2}$	is final mole of H_2O_2 in the sample analyzed by titration method

The volatility of benzene makes it difficult to completely avoid its loss by evaporation during the reaction as well as during the sample preparation. Due to this, the conventional direct calculation of benzene conversion based on its left amount after the reaction would lead to miscalculations. Therefore, benzene conversion in the present work is defined as the mole of benzene converts to reaction products. Since mole of the products (phenol, 1,4-benzoquinone, catechol and hydroquinone) are formed by one mole of benzene, their stochiometrical factors were simply one. The calculation is shown in equation **(3.9).**

$$C_{\text{Benzene}} = \frac{n_{\text{Phenol}} + n_{\text{1,4-Benzoquinone}} + n_{\text{Catechol}} + n_{\text{Hydroquinone}}}{n_{\text{0, Benzene}}} \times 100 \qquad \textbf{(3.9)}$$

Where;

C_{Benzene}	is benzene conversion (%)
$n_{\text{0, Benzene}}$	is initial mole of benzene

The product selectivity was calculated based on overall moles of produced products including phenol, 1,4-benzoquinone, catechol and hydroquinone as shown in equations **(3.10)**, **(3.11)**, **(3.12)** and **(3.13)**.

$$S_{\text{Phenol}} = \frac{n_{\text{Phenol}}}{n_{\text{Phenol}} + n_{\text{1,4-Benzoquinone}} + n_{\text{Catechol}} + n_{\text{Hydroquinone}}} \times 100 \qquad \textbf{(3.10)}$$

$$S_{\text{1,4-Benzoquinone}} = \frac{n_{\text{1,4-Benzoquinone}}}{n_{\text{Phenol}} + n_{\text{1,4-Benzoquinone}} + n_{\text{Catechol}} + n_{\text{Hydroquinone}}} \times 100 \qquad \textbf{(3.11)}$$

$$S_{\text{Catechol}} = \frac{n_{\text{Catechol}}}{n_{\text{Phenol}} + n_{\text{1,4-Benzoquinone}} + n_{\text{Catechol}} + n_{\text{Hydroquinone}}} \times 100 \qquad \textbf{(3.12)}$$

$$S_{\text{Hydroquinone}} = \frac{n_{\text{Hydroquinone}}}{n_{\text{Phenol}} + n_{\text{1,4-Benzoquinone}} + n_{\text{Catechol}} + n_{\text{Hydroquinone}}} \times 100 \qquad \textbf{(3.13)}$$

Where;

S_{Phenol}	is phenol selectivity (%)
$S_{\text{1,4−Benzoquinone}}$	is 1,4-benzoquinone selectivity (%)
S_{Catecol}	is catechol selectivity (%)
$S_{\text{Hydroquinone}}$	is hydroquinone selectivity (%)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst characterization

4.1.1 ICP-AES

Chemical compositions of TS-PQ^{TM} catalyst, synthesized TS-1 and synthesized Ti-MCM-41 catalysts were analyzed by ICP-AES. The results are presented in Table 4.1.

Table 4.1 Chemical compositions ratio by mole of catalyst samples.

Catalyst	**Si/Ti ratio**
TS-PQ^{TM}	46
TS-1	33
Ti-MCM-41	51

4.1.2 N_2 adsorption-desorption isotherm

N_2 adsorption-desorption isotherm of TS-PQ^{TM}, TS-1 and Ti-MCM-41 are shown in **Figures 4.1, 4.2** and **4.3**, respectively. The hysteresis loops generated by the capillary condensation of the adsorbate in the mesopores of the solid are presented in all materials. The presence of hysteresis loops in **Figures 4.1** and **4.2** for TS-PQ^{TM} and TS-1 indicates that these microporous materials do have part of mesopores similar to Ti-MCM-41 which is the mesoporous material and this part is substantially larger in the case of TS-PQ^{TM}.

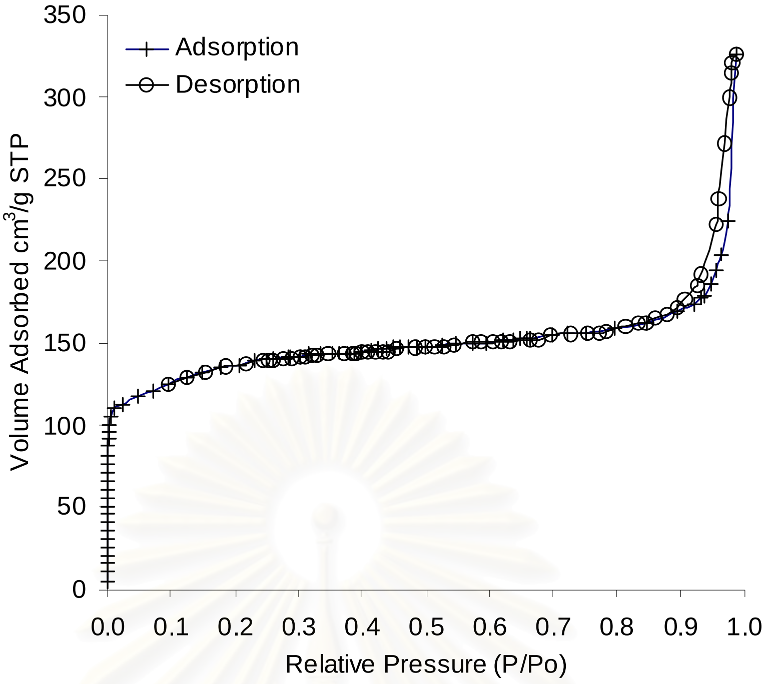


Figure 4.1 N_2 adsorption-desorption isotherm of TS-PQ^{TM} catalyst.

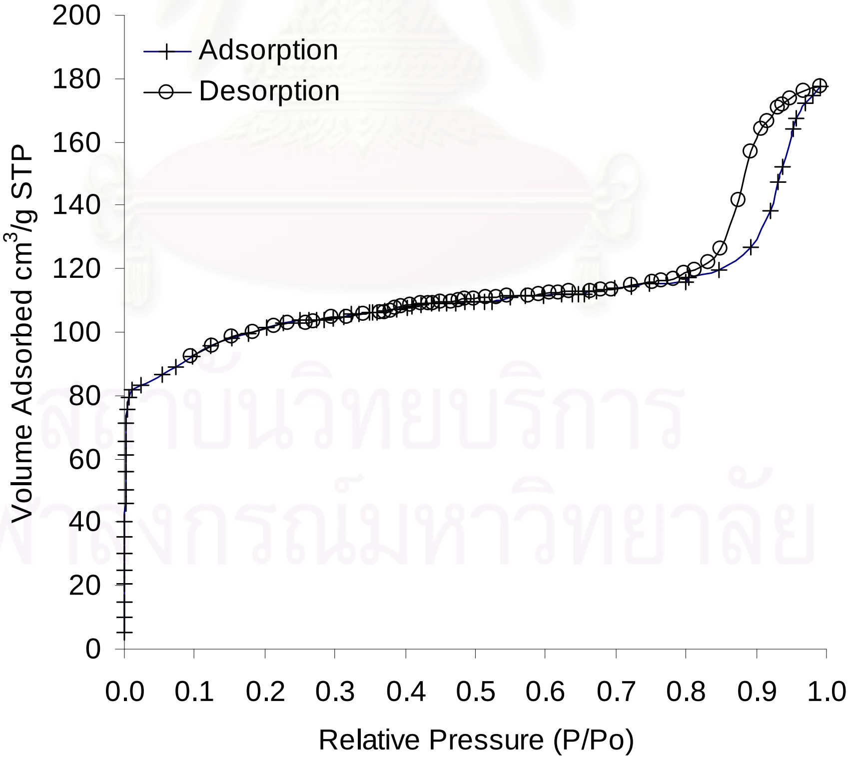


Figure 4.2 N_2 adsorption-desorption isotherm of TS-1 catalyst.

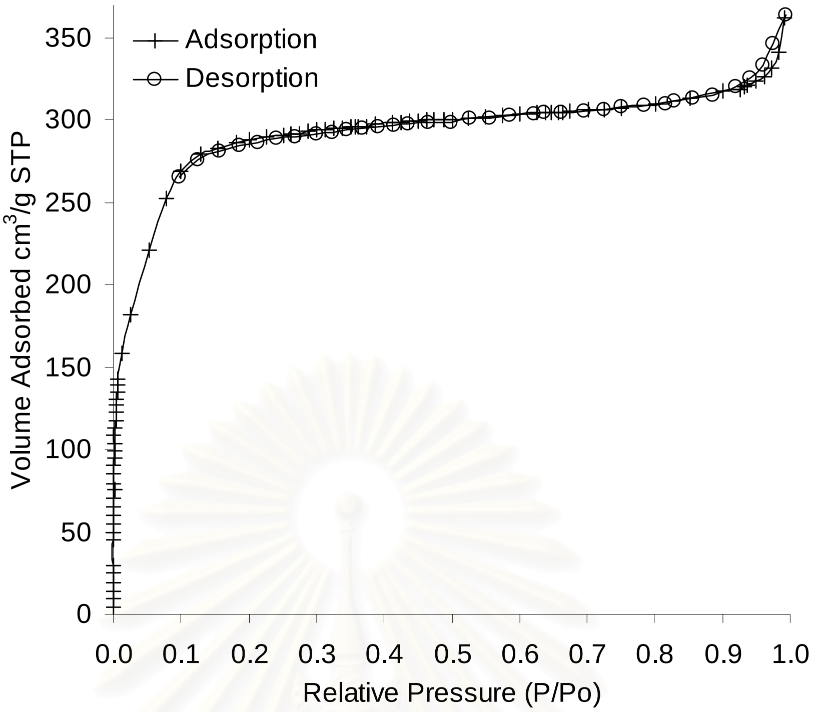


Figure 4.3 N_2 adsorption-desorption isotherm of Ti-MCM-41 catalyst.

The value of BET surface area, t-Plot micropore area, surface area of pores between 20 Å and 1000 Å and volume of pores between 20 Å and 1000 Å calculated from BJH method are given in **Table 4.2.** Horvath-Kawazoe which is the special model for microporous material was used to estimate the average micropore diameter of TS-PQ^{TM} and TS-1. Horvath-Kawazoe differential pore volume plots of TS-PQ^{TM} and TS-1 catalysts in **Figure 4.4** show that, both catalysts have similar average micropore diameter, around 5.5 Å close to the theory.

Table 4.2 The physical properties of the catalysts.

Sample	**BET surface area (m^2/g)**	**Micropore volume (cm^3/g)**	**Surface area of pores between 20 Å to1000 Å$^{(a)}$ (m^2/g)**	**Volume of pores between 20 Å to1000 Å$^{(b)}$ (cm^3/g)**
TS-PQ^{TM}	454	0.1167	81.83	0.31
TS-1	339	0.0846	63.67	0.14
Ti-MCM-41	965	-	87.22	0.15

(a) BJH Desorption cumulative surface area of pores between 20 Å and 1000 Å width
(b) BJH Desorption cumulative volume of pores between 20 Å and 1000 Å width

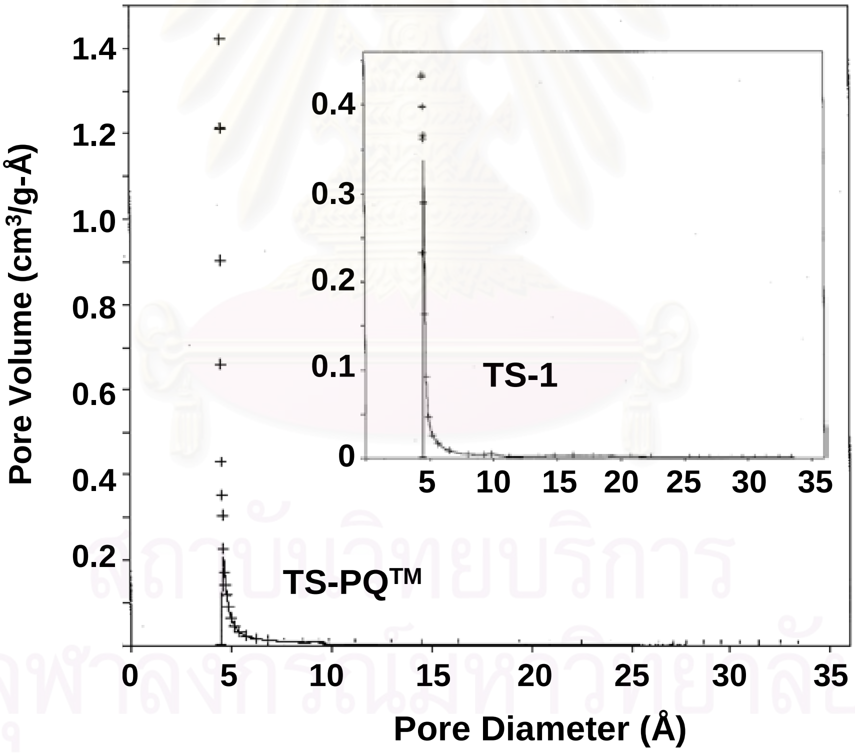


Figure 4.4 Horvath-Kawazoe differential pore volume plot of TS-PQ^{TM} and TS-1.

Ti-MCM-41 has more advantages over microporous material due to the accessibility of reactant molecule to the active sites [He *et al.*, 2001]. However, it could be realized from **Table 4.2** that TS-PQ^{TM} catalyst has not only high BET surface and high micropore volume, in addition it has the large part of mesopores presented in addition to the micropores resulting much higher surface area and volume of pores between 20 Å and 1000 Å comparison to TS-1 catalyst. These features should have an effect on the diffusion transport phenomena as well as a positive effect on the catalytic performance in particular higher activity in a three phase system.

4.1.3 XRD

The results of **Figure 4.5** and **4.6** show that TS-PQ^{TM} and TS-1 samples behave the typical MFI structure [Bengao *et al.*, 1998]. The XRD pattern of Ti-MCM-41 in **Figure 4.7** shows similar pattern from literature [Lin *et al.*, 2005].

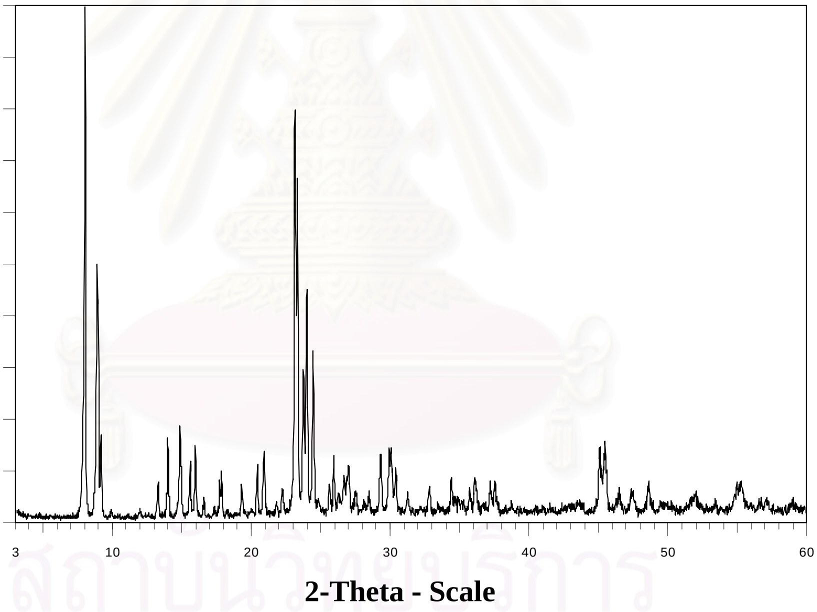


Figure 4.5 The XRD pattern of TS-PQ^{TM} catalyst.

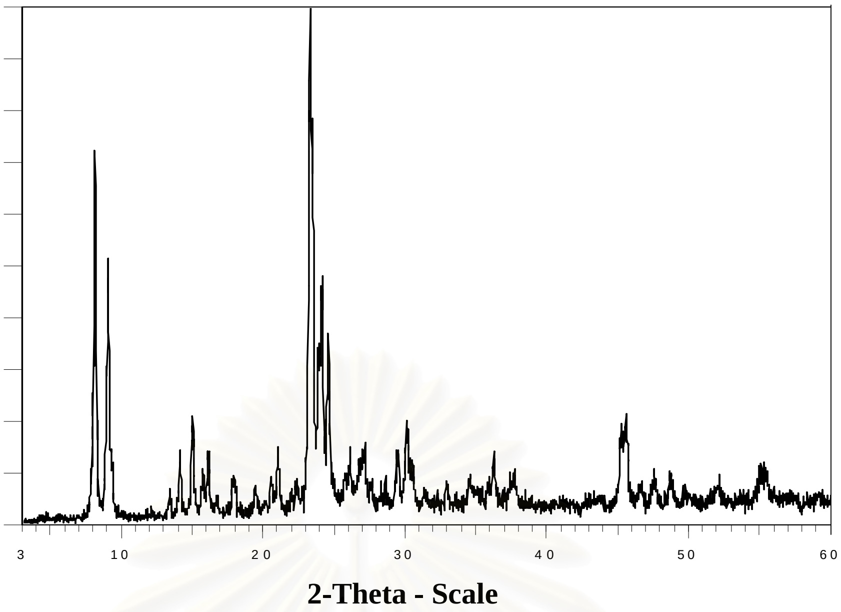


Figure 4.6 The XRD pattern of TS-1 catalyst.

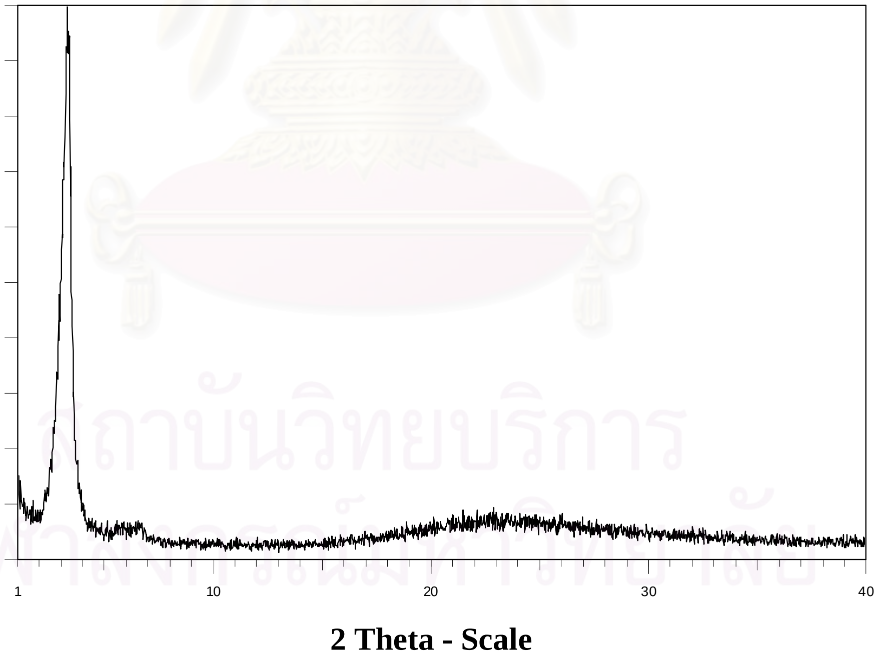


Figure 4.7 The XRD pattern of Ti-MCM-41 catalyst.

4.1.4 FT-IR

The FTIR spectra of TS-PQ^{TM}, TS-1 and Ti-MCM-41 in **Figures 4.8, 4.9** and **4.10** show the band around 960 cm^{-1}, representing titanium incorporated into silica framework [Bengoa *et al.*, 1998; , Halasz *et al.*, 2003a; Halasz *et al.*, 2003b; Senderov *et al.*, 2003]. For the MFI catalysts, the ratio of the intensity between 960 cm^{-1} and 800 cm^{-1} band calculated with the help of ORIGIN$^{®}$ program of TS-PQ^{TM} and TS-1 is 0.55 and 0.81, respectively. This ratio, which has been normally used as an indicator of the relative abundance of single Ti atom surrounded by Si atoms, indicates that the number of Ti atoms incorporated into framework of TS-1 catalyst is substantially higher than for TS-PQ^{TM}. The results are in agreement with the observed results from ICP-AES that the Ti content relatives to Si atom in TS-PQ^{TM} is lower than TS-1.

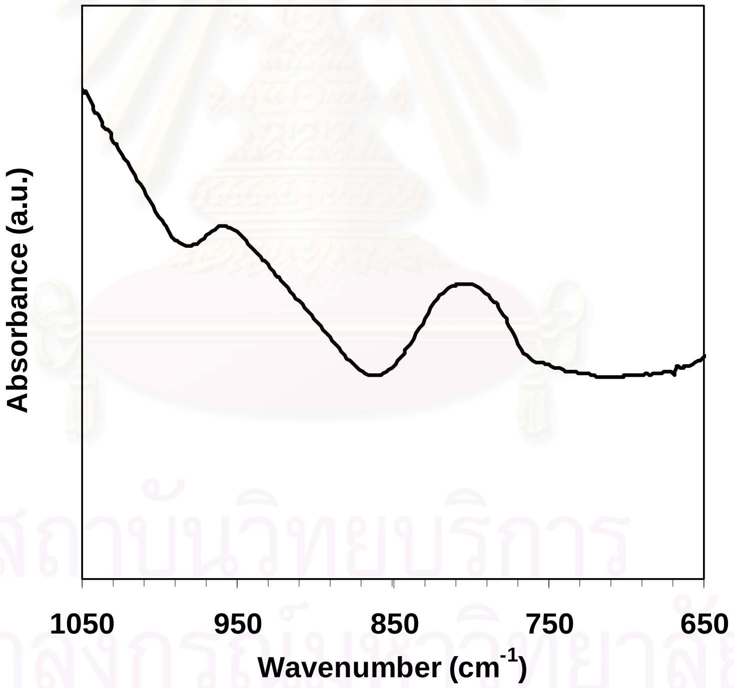


Figure 4.8 FT-IR spectra of TS-PQ^{TM} catalyst in the wave number range between 650 cm^{-1} and 1050 cm^{-1}.

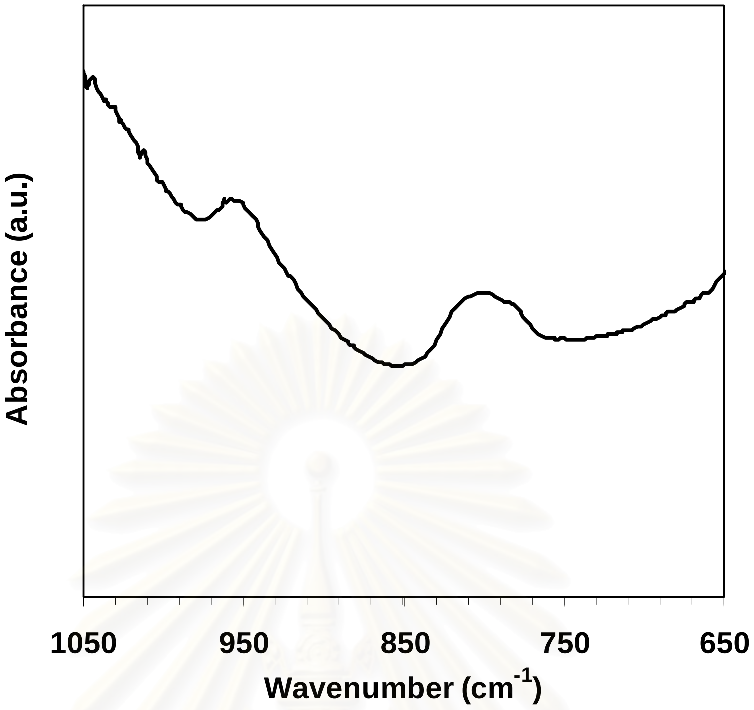


Figure 4.9 FT-IR spectra of TS-1 catalyst in the wave number range between 650 cm^{-1} and 1050 cm^{-1}.

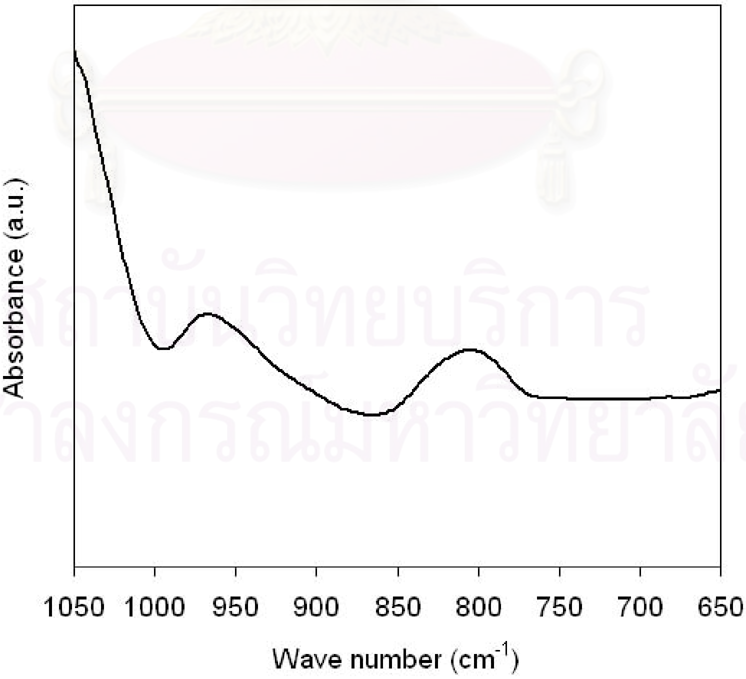


Figure 4.10 FT-IR spectra of Ti-MCM-41 catalyst in wave number range between 650 cm^{-1} and 1050 cm^{-1}.

The FT-IR spectra of the catalysts measured at room temperature in the wave number range between 1500 cm^{-1} and 4000 cm^{-1} are shown in **Figures 4.11, 4.12** and **4.13**. The spectra of TS-PQ^{TM} and Ti-MCM-41 showed the band around 3700 cm^{-1} representing the well-known stretching vibration of isolated terminal Si-OH groups [Halasz *et al.*, 2003]. In contrary, this band was not observed on TS-1 catalyst which is in agreement with the earlier report that the surface of TS-1 is more hydrophobic than the surface of Ti-MCM-41 [He *et al.*, 2001]. The Si-OH group containing in TS-PQ^{TM} should have a positive effect on the surface resulting in less hydrophobic surface than the typical TS-1 catalyst. In addition, TS-PQ^{TM} catalyst shows the intense broad band around 3500 cm^{-1} representing the molecular water and an array of hydrogen bonded hydroxyl groups [Bianchi *et al.*, 2007; Halasz *et al.*, 2003a; Halasz *et al.*, 2003b; Senderov *et al.*, 2003], while the spectra for TS-1 shows only small board peak in this band region. That is an indication that defects are present in the structure of TS-PQ^{TM}. Such defects improve the hydrophilicity on the catalyst surface and should have an influence on the catalytic performance.

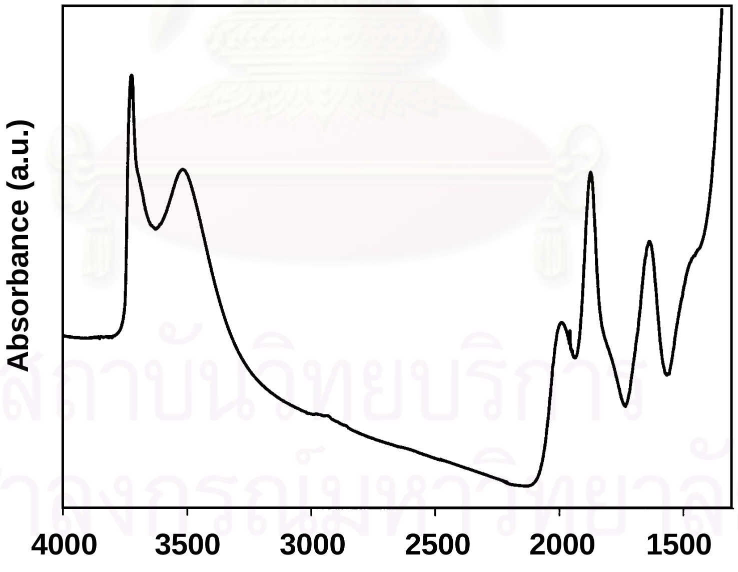


Figure 4.11 FT-IR spectra of TS-PQ^{TM} catalyst in wave number range between 1500 cm^{-1} and 4000 cm^{-1}.

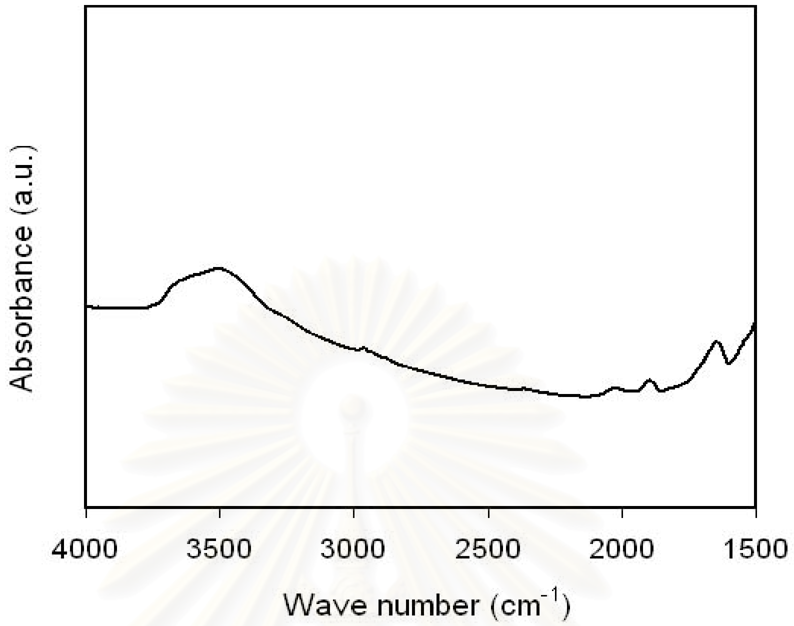


Figure 4.12 FT-IR spectra of TS-1 catalyst in wave number range between 1500 cm^{-1} and 4000 cm^{-1}.

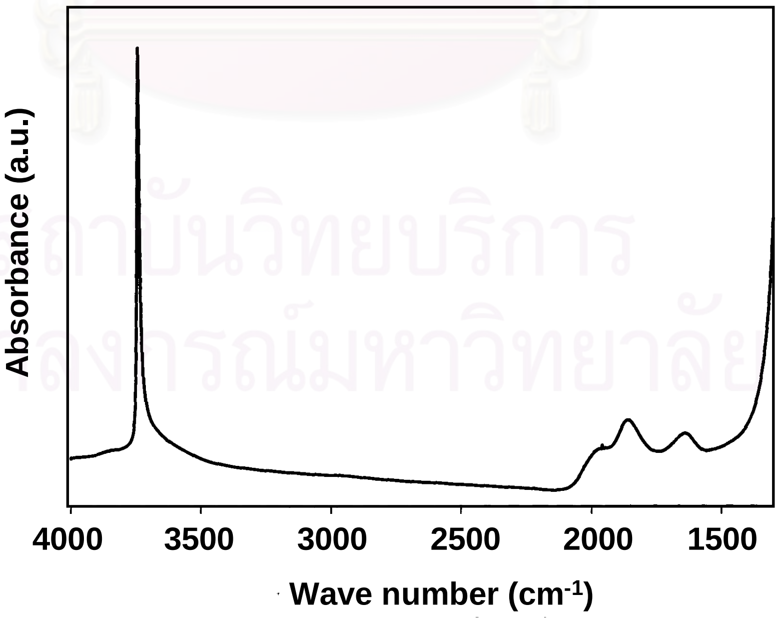


Figure 4.13 FT-IR spectra of Ti-MCM-41 catalyst in wave number range between 1500 cm^{-1} and 4000 cm^{-1}.

4.1.5 DRUV-Vis

The diffuse reflectance UV-Vis spectra of TS-PQ^{TM}, TS-1 and Ti-MCM-41 are shown in **Figures 4.14**, **4.15** and **4.16**, respectively. The spectra of the TS-1 and Ti-MCM-41 catalyst show only an absorption band at around 210 nm corresponding to isolated tetrahedral titanium atoms in the framework [Bhaumik *et al.*, 1998;, Balducci *et al.*, 2003; Bianchi *et al.*, 2007; Halasz *et al.*, 2003a; Halasz *et al.*, 2003b; Senderov *et al.*, 2003; Hu *et al.*, 2003; Serrano *et al.*, 2007; Hulea *et al.*, 2004] whereas the absence of a band around 260 nm to 360 nm indicates that these material are free of undesired TiO_2 phase [Bhaumik *et al.*, 1998; Hu *et al.*, 2003; Serrano *et al.*, 2007]. In contrast, TS-PQ^{TM} has an absorption band around 300 nm which could be extraframework Ti species [Wang *et al.*, 2007]. However, the DRUV-Vis spectra measured under ambient conditions did not show a band between 215 nm and 230 nm which was observed in the same material under evacuation to 3×10^{-3} Pa at 400°C as shown in **Figure 4.17**. Under those conditions, TS-PQ^{TM} clearly showed a substantial UV absorption mainly above 220 nm. This indicates that, TS-PQ^{TM} catalyst does not contain only isolated tetrahedral Ti^{4+} ions in lattice positions unlike TS-1. The band in this range is assigned to isolated monometric Ti with coordination more than tetrahedral and probably responsible for the superior in catalytic properties of TS-PQ^{TM} catalyst comparison to TS-1 catalyst in the oxyfunctionalization of *n*-hexane in the previous work [Senderov *et al.*, 2005].

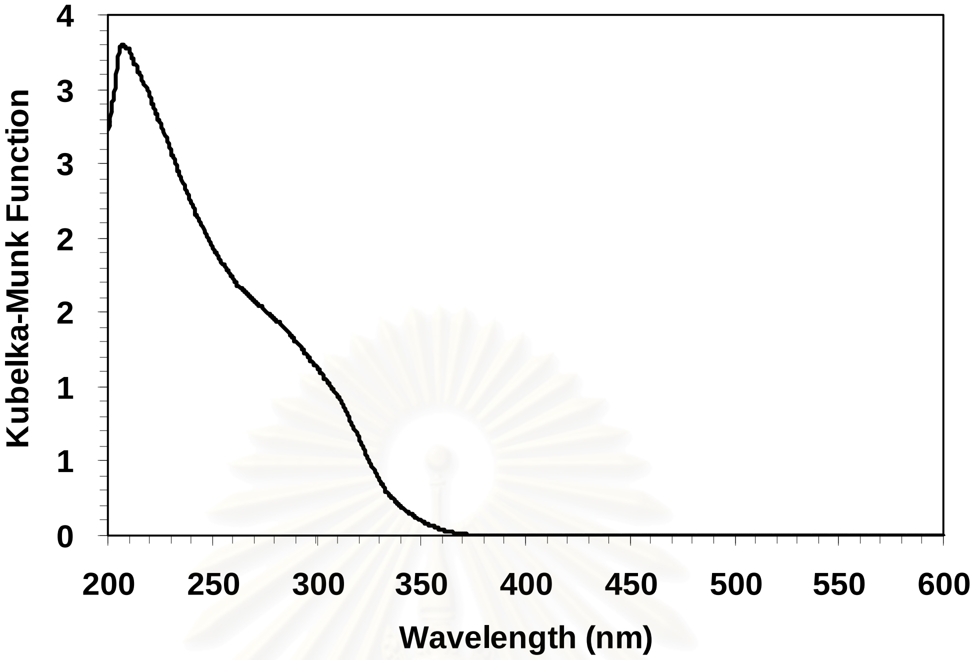


Figure 4.14 Diffuse reflectance UV-Vis spectra of TS-PQ^{TM} catalyst.

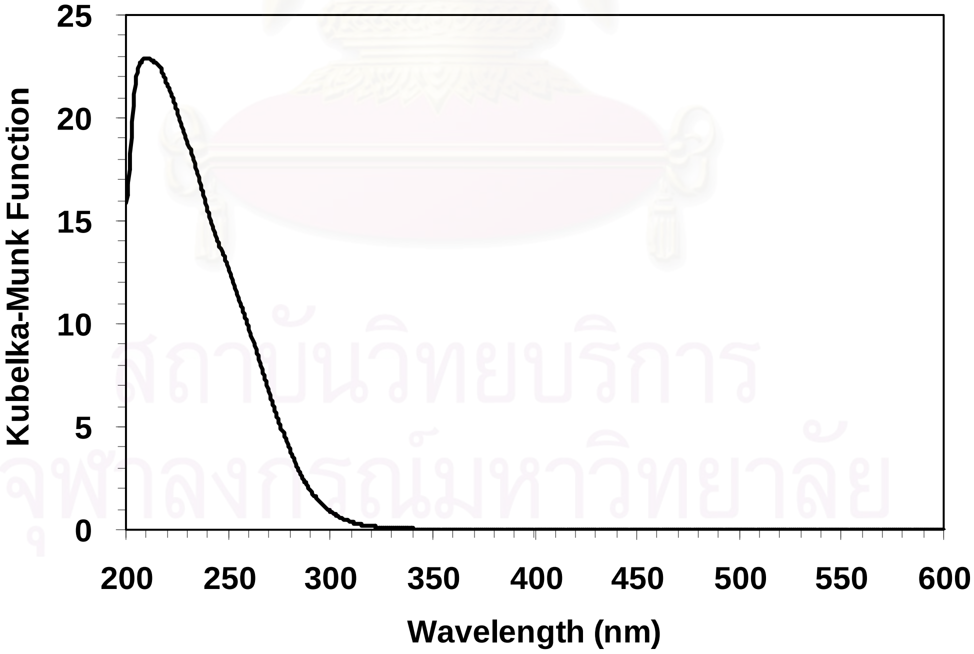


Figure 4.15 Diffuse reflectance UV-Vis spectra of TS-1 catalyst.

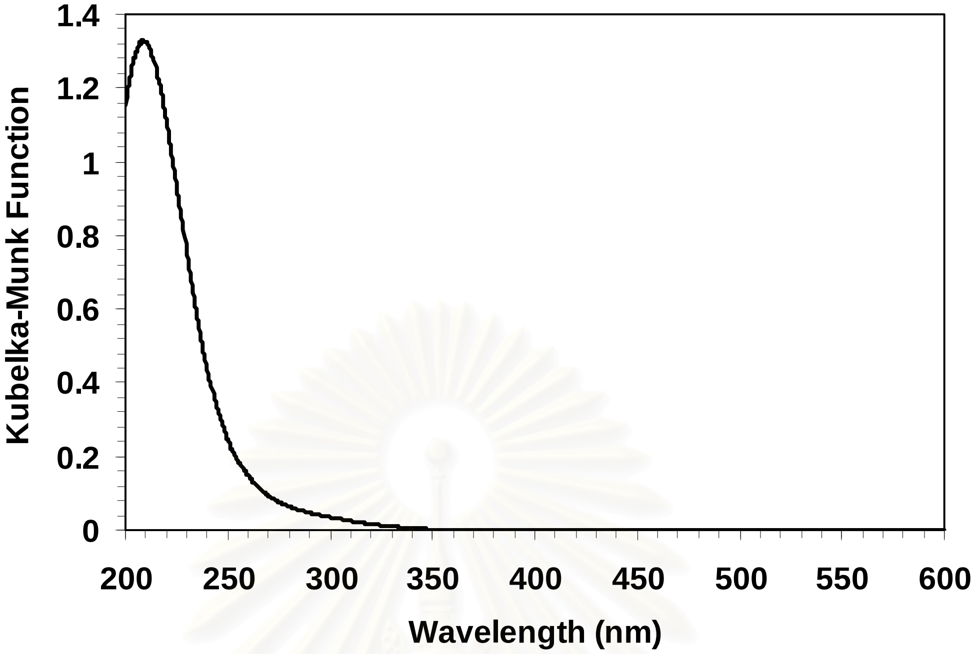


Figure 4.16 Diffuse reflectance UV-Vis spectra of Ti-MCM-41 catalyst.

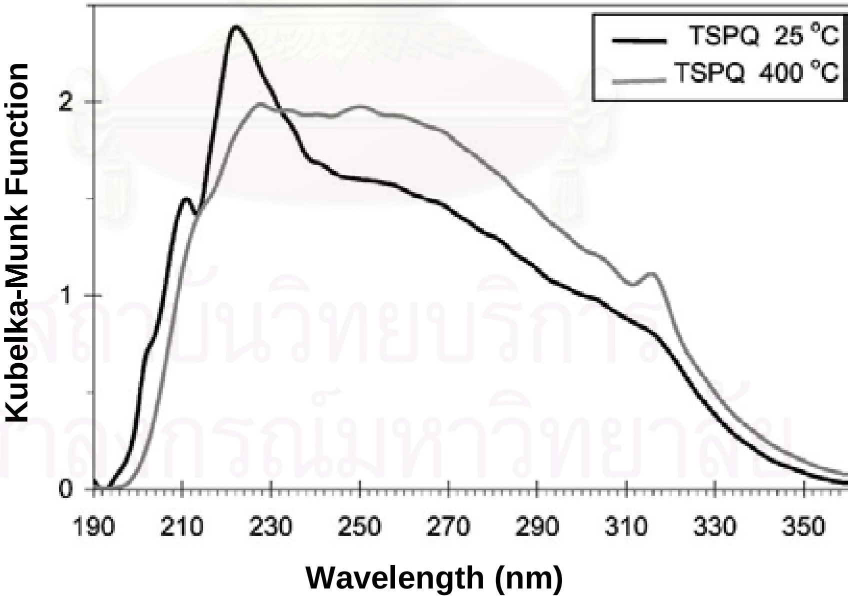


Figure 4.17 FT-UV–DRIFT spectra of TS-PQ™ silicate after evacuation at 3×10^{-3} Pa at 25°C and 400°C (given by Halasz *et al.*, 2003a)

4.1.6 SEM

Figures 4.18 and **4.19** present the scanning electron micrographs of TS-PQ^{TM} and TS-1, respectively. It is clearly showed that TS-PQ^{TM} is not highly crystallized which might due to the structure defects of the catalyst. The crystalline morphology of TS-PQ^{TM} is nearly in spherical shape while TS-1 shows a cubic shape. The particle size of TS-PQ^{TM} is around 100 nm to 300 nm, much smaller than TS-1 which has the average particle size greater that 2 µm. However, the particle size for TS-1 material in this work is different from the previous work which reported TS-1 particle size around 200 nm under the same preparation procedure [Bhaumik *et al*., 1998]. This might be ascribed to the difference of crystallization system. The small particle size of TS-PQ^{TM} can contribute to the high surface area and pore volume and that should have an influence on the catalytic performance. SEM picture of Ti-MCM-41 in **Figure 4.20** shows than the catalyst is in amorphous phase which is the typical property of Ti-MCM-41 mesoporous material.

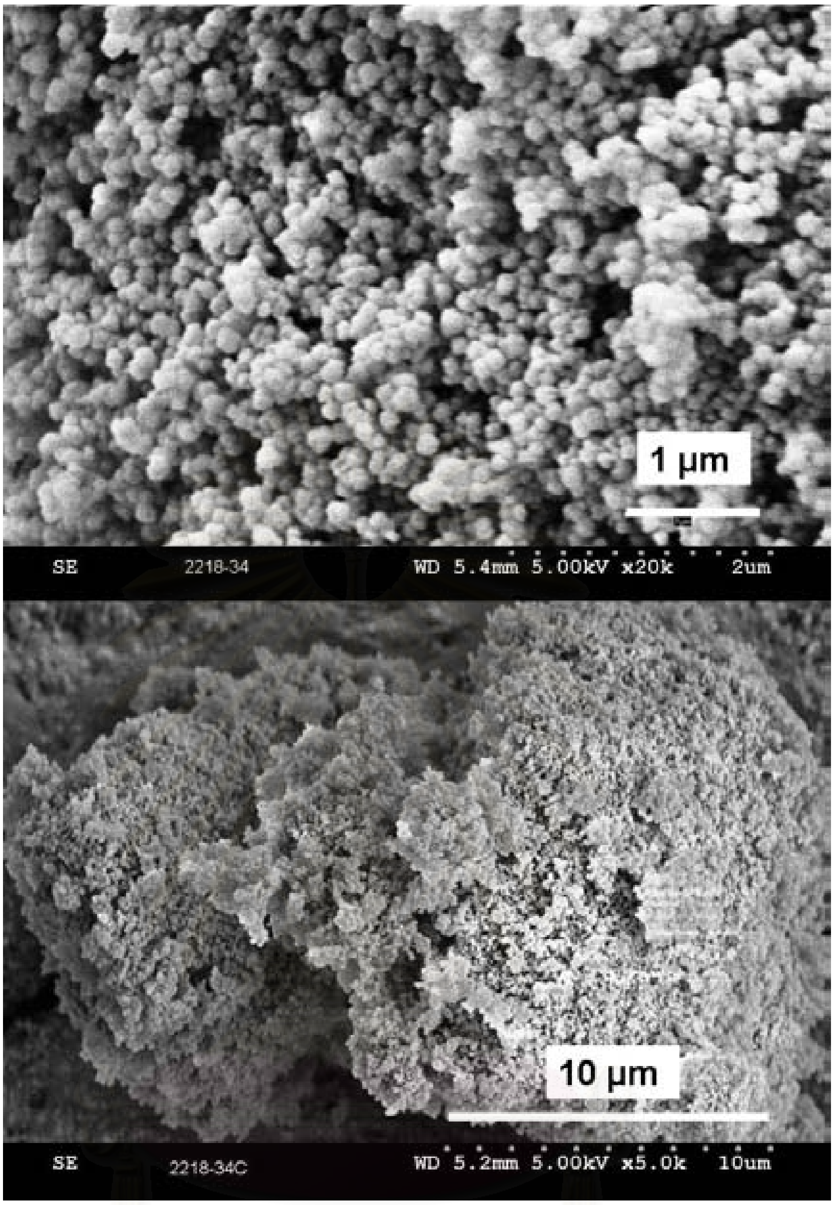


Figure 4.18 SEM micrographs of TS-PQ^{TM} catalyst.

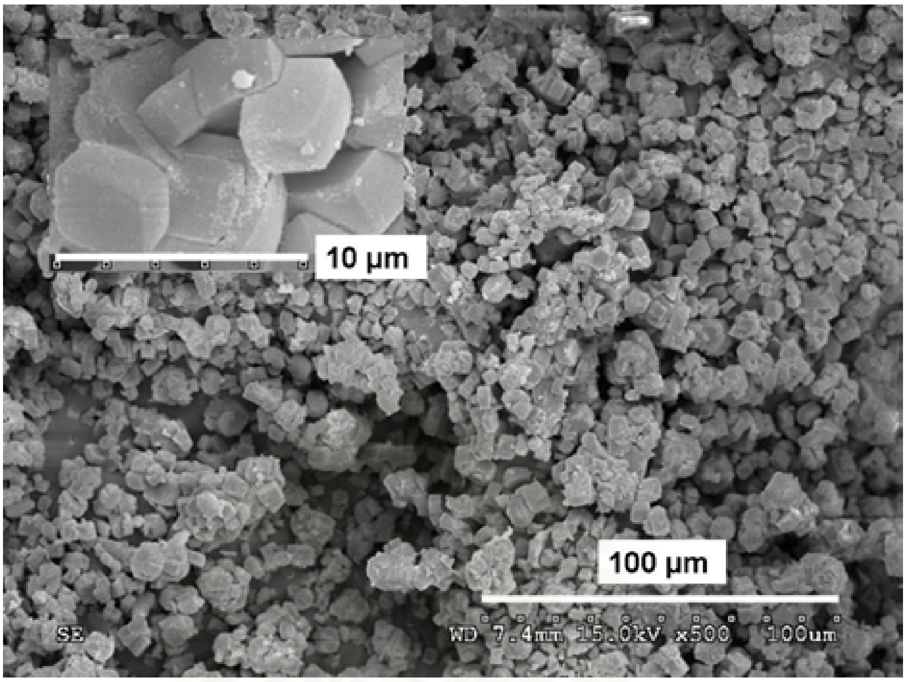


Figure 4.19 SEM micrographs of TS-1 catalyst.

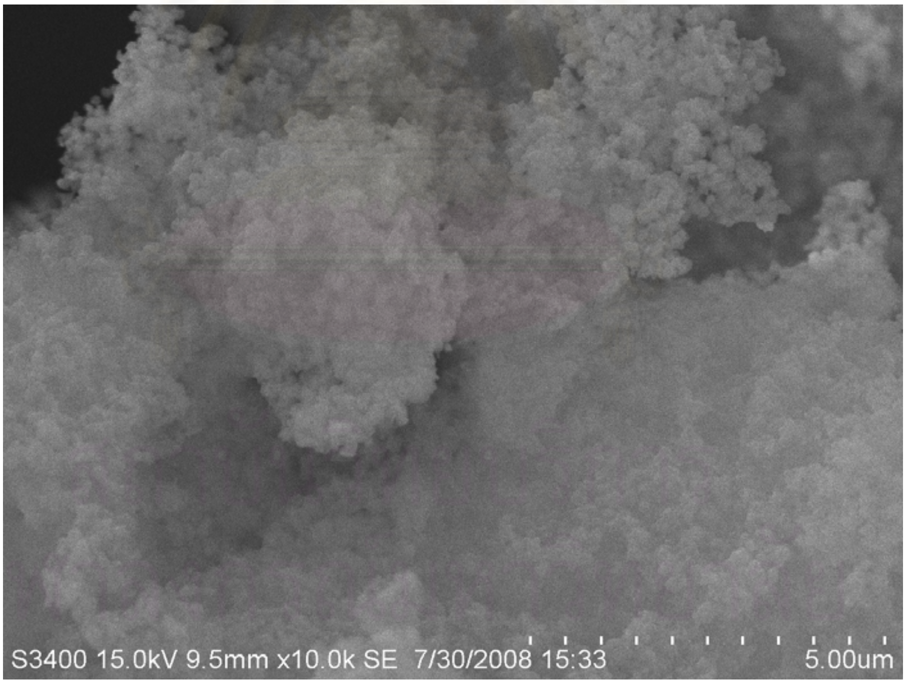


Figure 4.20 SEM micrographs of Ti-MCM-41 catalyst.

4.2 Catalytic reaction

The selective oxidation of benzene was performed in the typical batch glass reactor excepting the study of the pressure effect where the experiments were carried out in the autoclave. The titration of H_2O_2 by potassium permanganate was performed but it was not accomplished due to the interference of organic compounds in the mixture. Therefore, the H_2O_2 conversion to organic compounds ($C_{H_2O_2,\ Org.}$) was reported instead on the total conversion of H_2O_2 ($C_{H_2O_2}$). Phenol selectivity, 1,4-benzoquinone selectivity, catechol selectivity and hydroquinone selectivity were calculated using equations **(3.10)**, **(3.11)**, **(3.12**) and **(3.13)**, respectively.

4.2.1 The preliminary study of the selective oxidation of benzene using H_2O_2 under two-phase and three-phase system over titanium-silica based catalyst

The activity of various catalysts from the literatures and preliminary study of TS-PQ^{TM} catalyst under two-phase system and tree-phase system (solvent-free system) are listed in **Table 4.3**.

Table 4.3 Comparison of the catalytic performance of various catalysts under two-phase and three-phase system (solvent-free system).

Co-Solvent	**Catalyst**	**Conversion (%)**	**S_{Phenol} (%)**	**Reference**
Acetone	TS-1$^{(a)}$	4.2	41	Bianchi *et al.*, 2007
	TS-1$^{(b)}$	10	63	He *et al.*, 2001
	TS-PQ$^{TM(c)}$	0.59$^{(k)}$	53.61	***Present work***
Acetonitrile	TS-1$^{(a)}$	4.5	43	Bianchi *et al.*, 2007
	TS-1$^{(d)}$	11.6	82	Bhaumik *et al.*, 1998
	V/MCM-41$^{(e)}$	13.0	48	Chen and Lu, 1999
	TS-PQ$^{TM(c)}$	0.31$^{(k)}$	56	***Present work***
Methanol	TS-1$^{(a)}$	4.7	40	Bianchi *et al.*, 2007
	TS-PQ$^{TM(c)}$	0.53$^{(k)}$	78	***Present work***
Acetic acid	TS-1$^{(a)}$	5.1	50	Bianchi *et al.*, 2007
	TS-1$^{(f)}$	5.3	97	Gao and Xu, 2006
	V/MCM-41$^{(g)}$	10.8	67	Lemke *et al.*, 2003
	V/Clay$^{(h)}$	14.1	93.9	Gao and Xu, 2006
tert-butyl alcohol	TS-1$^{(a)}$	4.1	44	Bianchi *et al.*, 2007
	TS-PQ$^{TM(c)}$	1.2$^{(k)}$	91	***Present work***
Sulfolane	TS-1$^{(a)}$	7.8	83	Bianchi *et al.*, 2007
Solvent-free	TS-1$^{(a)}$	4.5	42	Bianchi *et al.*, 2007
	TS-1$^{(a)}$	3.5	>99	***Present work***
	TS-1$^{(a)}$	74.4	85.6	Bhaumik *et al.*, 1998
	TS-1$^{(j)}$	8.5	65.6	Yokoi *et al.*, 2003
	TS-1$^{(i)}$	17$^{(k)}$	74	Bengao *et al.*, 1998
	Ti-MCM-41$^{(c)}$	<0.01	100	***Present work***
	TS-1$^{(c)}$	1$^{(k)}$	74	***Present work***
	TS-PQ$^{TM(c)}$	19.4$^{(k)}$	92	***Present work***

(a) Reaction conditions; Benzene/co-solvent =2/8 wt/wt, H_2O_2:benzene molar ratio = 0.1, TS-1/benzene= 0.1 wt/wt at 100°C.

(b) Reaction conditions; 0.1 g TS-1, benzene 35 g, H_2O_2 15 g, acetone 15 g, Benzene:H_2O_2:solvent molar ratio= 1:3:5.7 at 65°C for 3 h.

(c) Reaction conditions; 0.2 g of catalyst, 0.056 mol of benzene and 0.011 mol of H_2O_2 (30 wt.%) in 20 ml solvent or water, at 70°C for 3 h.

(d) Reaction conditions; Benzene:acetronitrile:TS-1 = 1:5:0.15 (wt/wt), benzene:H_2O_2= 1.0 molar ratio at 60°C for 8 h.

(e) Reaction conditions; 10 mmol benzene and 30 mmol H_2O_2 in 6 ml acetronitrile at 60°C for 3 h.

(f) Reaction conditions; 1 g of TS-1 catalyst, 0.056 mmol benzene, 0.098 mmol H_2O_2 in 30 ml of acetic acid at 40°C for 4 h.

(g) Reaction conditions; 4 mmol benzene, 4 mmol H_2O_2 in acetic acid at 22°C for 20 h.

(h) Reaction conditions; 1.4 benzene:H_2O_2 molar ratio in 30 ml of acetic acid at 40°C for 4 h, 0.25 g of catalyst weight, 2.5% of vanadium loading.

(i) Reaction conditions; 1.5 g of TS-1 catalyst, 90 ml of benzene and 9 ml of H_2O_2 (30 wt.%), 30°C for 6 h.

(j) Reaction conditions; 5 mmol benzene, 2.5 mmol H_2O_2, 50 g of TS-1 catalyst, H_2O 10 ml at 60°C for 1 h.

(k) The conversion was calculated based on H_2O_2 converted to organic compounds.

From **Table 4.3**, TS-PQ^{TM} catalyst exhibited poor conversion comparison to TS-1 and vanadium containing catalyst from the literature in the two phase systems. Among the catalysts in those previous works, clay supported vanadium catalyst show the remarkable catalytic activity with high phenol selectivity using acetic acid as solvent. Nevertheless, acetic acid is corrosive and not preferable in industrial application. In solvent-free system, Ti-MCM-41 exhibited very poor performance. The use of TS-PQ^{TM} catalyst results in higher H_2O_2 conversion to organic compounds although the reaction conditions were identical with those of TS-1. Although, 74.4% maximum benzene conversion was reported over TS-1 catalyst [Bhaumik *et al*., 1998] but such excellence conversion could not be reproduced by Bianchi *et al*. in 2007 and by the present work under identical conditions. Another remarkable catalytic activity in the three phase system was reported by Bengoa *et al.* over TS-1 catalyst in 1998. The performance of the catalyst based on H_2O_2 calculation basis was comparable to TS-PQ^{TM} catalyst in preliminary study but the phenol selectivity was still lower than that achieved over TS-PQ^{TM}.

From the product analysis and conversion calculation point of view, many researchers have analyzed and reported the catalytic activity in different ways. Most of the publications showed the results in term of benzene conversion. In fact that benzene is a volatile organic compound, the volatility of benzene makes it difficult to completely avoid its loss by evaporation during the reaction under atmospheric pressure. The conventional direct calculation of benzene conversion based on its left amount after the reaction would lead to an unbalance between benzene reactant and products. Some researchers have evaluated the benzene conversion by considering the produced products instead of reacted benzene. In such case, all of the products have to be quantitatively identified and the analytical method becomes crucial.

In the case that H_2O_2 is present in reaction mixture, it is possible that the reaction can also take place inside GC column during the analysis. In 1993, Van der Pol *et al*. found that hydroquinone product can further react with H_2O_2 to form 1,4-benzoquinone inside the GC column. Due to such kind of reaction, a misleading determination of the product selectivity can be caused [Martens *et al*., 1993; Van der Pol *et al*., 1993]. Even though the HPLC analysis is a recommended technique for the analysis but that was considered as unnecessary due to the sample preparation in this study, where H_2O_2 was destroyed with manganese oxide prior to analysis. As long as there is a very low amount of H_2O_2 or no H_2O_2 in the sample, GC analysis gives the result in high accuracy as by means of HPLC.

The excellent performance of TS-PQ^{TM} is a result due to its physical surface properties such as higher BET surface, higher pore volume, higher proportion of mesopores and larger diameter of those mesopores. The presence of hydrogen bonded hydroxyls groups and Si-OH group in FT-IR spectra (**Figure 4.11**), assumably means more hydrophilic character than in the case of TS-1. Hydrophilicity facilitates the adsorption of H_2O_2. Furthermore, its high amount of mesopores part compared with TS-1 reduces the diffusion limitations in particular in a three phase system.

In addition, it has been proposed recently for TS-1 material that co-solvent in needed in order to help H_2O_2 molecules to hydrolyze Ti-O-Si bonds and to stabilize the generated lattice defects as active site [Clerici, 2001]. On the other hand, the distorted structure of this material might activate H_2O_2 without the need of hydrolyzing Ti-O-Si bond [Halasz *et al.*, 2003a]. In the case of TS-PQ^{TM}, the catalyst does not contain only isolated tetrahedral Ti^{4+} ions in lattice positions unlike defect-free TS-1. The structure of this catalyst has been distorted by none isomorphously substituted titanium ions and other structure defects leading to better catalytic performance even in the absence of a solvent. Moreover, TS-PQ^{TM} showed a better catalytic activity even though it is not so highly crystallized compared to TS-1.

In the three-phase system, the ability of the reactants to adsorb on the active sites also on defect sites is particularly important. From the polarity of benzene and H_2O_2 molecules, one can assume that benzene molecules have greater affinity to a hydrophobic surface while, in contrast, H_2O_2 molecules have a preferred affinity to a hydrophilic surface. In the absence of a solvent, hydrogen peroxide is easier adsorbed on the hydrophilic surface and coordinates with Ti by replacing a Ti-O-Si bond to form reactive oxo-titanium species [Srinivas *et al.*, 2003; Ratnasamy *et al.*, 2004]. Presumably such oxo-titanium species facilitate the direct insertion of oxygen into a benzene ring to form phenol [Thangaraj *et al.*, 1990]. The consecutive oxidation of phenol to yield 1,4-benzoquinone, hydroquinone or catechol has been postulated via the same mechanism.

The competitive advantage of adsorption of benzene over hydrogen peroxide hinders the formation of activated hydrogen peroxide. This can be compensated by the reduction of diffusion hindrance under the existence of mesopores and higher average pore diameter. However, the differences in pore diameter and hydrophilicity are presumably not only the reasons for good performance of the catalyst. TS-PQ^{TM} catalyst also exhibited much higher in activity comparison to the mesopore material, Ti-MCM-41 in solvent free system. This can be contributed to isolated monometric Ti with coordination more than tetrahedral and probably responsible for the superior in catalytic properties of TS-PQ^{TM}.

4.2.2 Optimization of the reaction condition over TS-PQ^{TM} catalyst under three-phase system

4.2.2.1 The effect of pressure on the conversion of H_2O_2 to organic compounds and product selectivity

The effect of pressure was investigated in autoclave using N_2 to pressurize the system. The molar ratio between benzene/H_2O_2 (30 wt. % aqueous solution) was 5:1. Benzene and H_2O_2 were added together before closing the reactor. The reaction temperature was studied at 60°C and 70°C under its own pressure and 20 bar of N_2. The amount of catalyst was 0.2 g and the stirring speed was 1100 rpm. The results in **Figure 4.21** show that pressure did not have a significant effect to the H_2O_2 conversion to organic compounds. In all cases, only slight conversion was observed. Only phenol was detected as product. The obtained conversions from the experiments in autoclave were lower than the results from the preliminary study with round bottom flask possibly owing to a limit of reactor size.

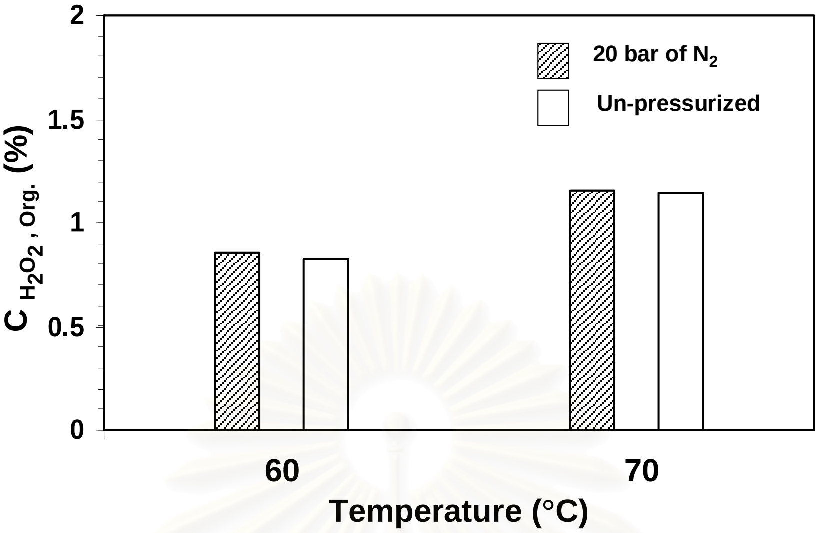


Figure 4.21 H_2O_2 conversion to organic compounds as a function of temperature in the selective oxidation of benzene catalyzed by TS-PQ^{TM} catalyst. Reaction conditions: Catalyst 0.2 gram, 0.011 mole of H_2O_2 and 0.056 mole of benzene, stirring speed 500 rpm.

4.2.2.2 The effect of H_2O_2 additional rate, temperature and stirring speed on the conversion of H_2O_2 to organic compounds and product selectivity

Table 4.4 illustrates the conversion of H_2O_2 to organic compounds and product selectivity at different reaction temperatures, stirring speeds and periods of H_2O_2 addition. At 70°C, H_2O_2 solution was slowly added drop-wise to the reactor with the help of an appropriate syringe during the first 10 min, 35 min and 75 min of the reaction. The results in **Table 4.4** do not show any remarkable effect on the conversion and phenol selectivity was obtained around 95% in all cases. At the same temperature, the reactions were performed at the stirring speeds of 500 rpm, 900 rpm and 1100 rpm and H_2O_2 was added in the first 10 min of the reaction. The best conversion was obtained at 1100 rpm stirring speed which is the maximum speed of the apparatus. Phenol was produced as major product at more than 90% selectivity with minor extent of 1,4-benzoquinone, hydroquinone and catechol.

The effect of temperature was investigated in the temperature range between 65°C and 75°C by fixing the stirring speed at 1100 rpm and adding H_2O_2 in the first 10 min of the reaction. The conversion increased to almost 20% with the increase of reaction temperature in this narrow range but slightly dropped at 75°C, presumably due to spontaneous decomposition of hydrogen peroxide. Thus the reaction temperature, 75°C appears to be the optimum temperature under the present reaction conditions.

Table 4.4 The effect of temperature, stirring speed and H_2O_2 additional rate on the conversion

Temperature (°C)	**Stirring speed (rpm)**	**Period of H_2O_2 addition (min)**	$C_{H_2O_2,\ Org.}$ **(%)**
70	500	70	13.9
70	500	35	13.4
70	500	10	14.9
70	900	10	17.3
70	1100	10	19.4
65	1100	10	14.9
75	1100	10	17.9

Reaction conditions: 0.056 mol of benzene and 0.011 mol of H_2O_2, 0.2 gram of TS-PQ^{TM} catalyst, 20 ml additional water, reaction time 3 h.

4.2.2.3 The effect of molar ratio between benzene/H_2O_2 on the conversion of H_2O_2 to organic compounds and product selectivity

The effect of molar ratio of benzene/H_2O_2 was studied at an adjusted H_2O_2 concentration and various molar amounts of benzene. In **Figure 4.22**, H_2O_2 conversion to organic compounds and product selectivity are plotted as a function of the benzene/H_2O_2 molar ratios. H_2O_2 conversion increased with the increase of benzene/H_2O_2 molar ratio up to 5:1, reaching a maximum of around 19% and remained at this level even though the molar ratio was further increased up to 10:1. The phenol selectivity was around 86-92%. Smaller amounts of other products including in quantitative order 1,4-benzoquinone, hydroquinone and catechol have been observed .

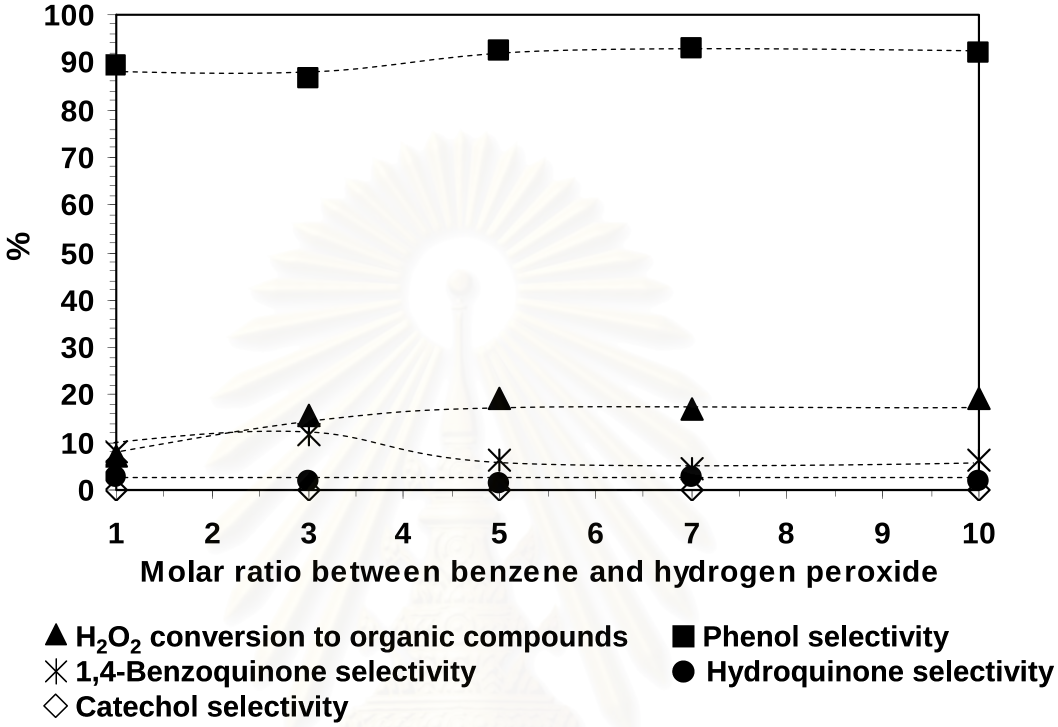


Figure 4.22 H_2O_2 conversion to organic compounds and product selectivity as a function of molar ratio of benzene/H_2O_2 in the selective oxidation of benzene catalyzed by TS-PQ^{TM}. Reaction conditions : atmospheric pressure, temperature 70°C, catalyst 0.2 g, 0.011 mole of H_2O_2 and x mole of benzene (x = 0.011, 0.034, 0.056, 0.079 and 0.113 mole), 20 ml additional water, stirring speed 1100 rpm, reaction time 3 h.

It might be predicted from these results that the steps of reaction are in following; the absorption and reaction of H_2O_2 to form active oxygen species on the catalyst surface, the diffusion of benzene through water phase to the catalyst surface, the reaction of benzene and active oxygen species to form phenol. If the amount of benzene in the reaction mixture is high, it would increase the opportunity of benzene molecules to reach the active species on active sites and form hydroxyl products. After the molar ratio of 5:1, the rate controlling step might change from the diffusion of benzene to the production of active oxygen species on the surface. Therefore, the optimum benzene/H_2O_2 ration under the studied conditions is 5:1.

4.2.2.4 The effect of volume of additional water on the conversion of H_2O_2 to organic compounds and product selectivity

Figure 4.23 illustrates the effect of additional water to the reaction mixture on H_2O_2 conversion to organic compounds and product selectivity. To increase the volume of additional water was found to enhance the conversion of H_2O_2, reaching 22% at 40 ml additional water. Thereby, phenol selectivity of 96% could be achieved. 60 ml additional water, however, caused a slight activity drop but increased phenol selectivity up to 98%. Blank experiments in the absence of H_2O_2 indicated that there is no direct reaction under these conditions between benzene and H_2O or phenol and water.

Water is believed to strip phenol away from the catalytically active sites, thereby preventing further oxidation of phenol. Moreover, it enables the formation of catalyst suspension and thereby the interaction of the three phases. On the other hand, the conversion of H_2O_2 to organic compounds decreased if the mixture was diluted with more than 60 ml of water. This drop should be due to insufficient rate of mixing thus to decrease diffusion rate of benzene and H_2O_2 molecules to the catalytic active sites.

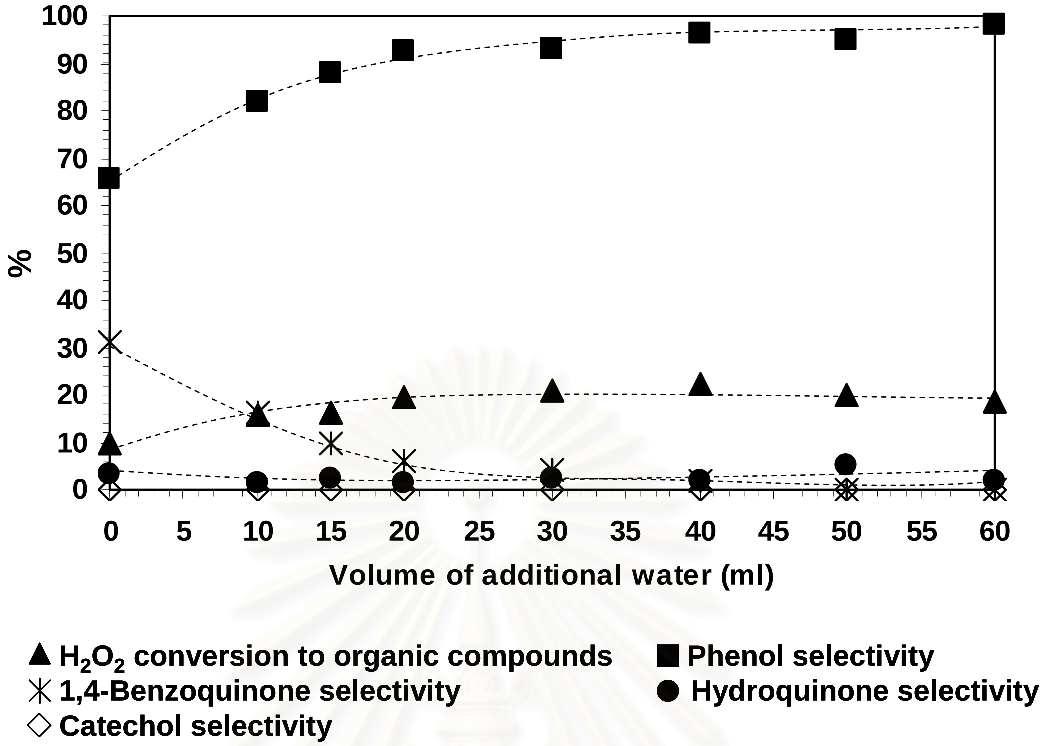


Figure 4.23 H_2O_2 conversion to organic compounds and product selectivity as a function of additional water in the selective oxidation of benzene catalyzed by TS-PQ^{TM}. Reaction conditions: atmospheric pressure, temperature 70°C, catalyst 0.2 g, 0.011 mole of H_2O_2 and 0.056 mole of benzene, stirring speed 1100 rpm, reaction time 3 h.

4.2.2.5 The effect of catalyst weight on the conversion of H_2O_2 to organic compounds and product selectivity

Figure 4.24 illustrates the effect of catalyst weight on the conversion of H_2O_2 to organic compounds and product selectivity. H_2O_2 conversion increased up to a maximum around 95% when the catalyst amount was 7 times higher than the initial amount. Unfortunately, in contrast the phenol selectivity decreased by further phenol oxydation to dihydroxylated products. At 1.5 g catalyst, only around 55 % phenol selectivity was observed. Among the by-products 1,4-benzoquinone first rose then dropped to almost zero. At the same time both the hydroquinone and catechol production increased. These results may be taken as evidence that the observed around 19% H_2O_2 conversion to organic compounds under the preliminary conditions was due to the lack of active sites and not due to the decomposition of H_2O_2. In the case of 19% H_2O_2 conversion, there is still about 80% of initial H_2O_2 left in the reaction mixture and the conversion can be elevated up to more than 95% by increasing the amount of catalyst. Such high conversions of H_2O_2 to organic compounds would not be possible if H_2O_2 would be decomposed to a larger extent. Further increase of the amount of catalyst from about 1.5 to 2.5 g did not cause any significant changes. It suggested that the H_2O_2 conversion to organic compounds has reached its maximum utilization and the remaining part might be decomposed.

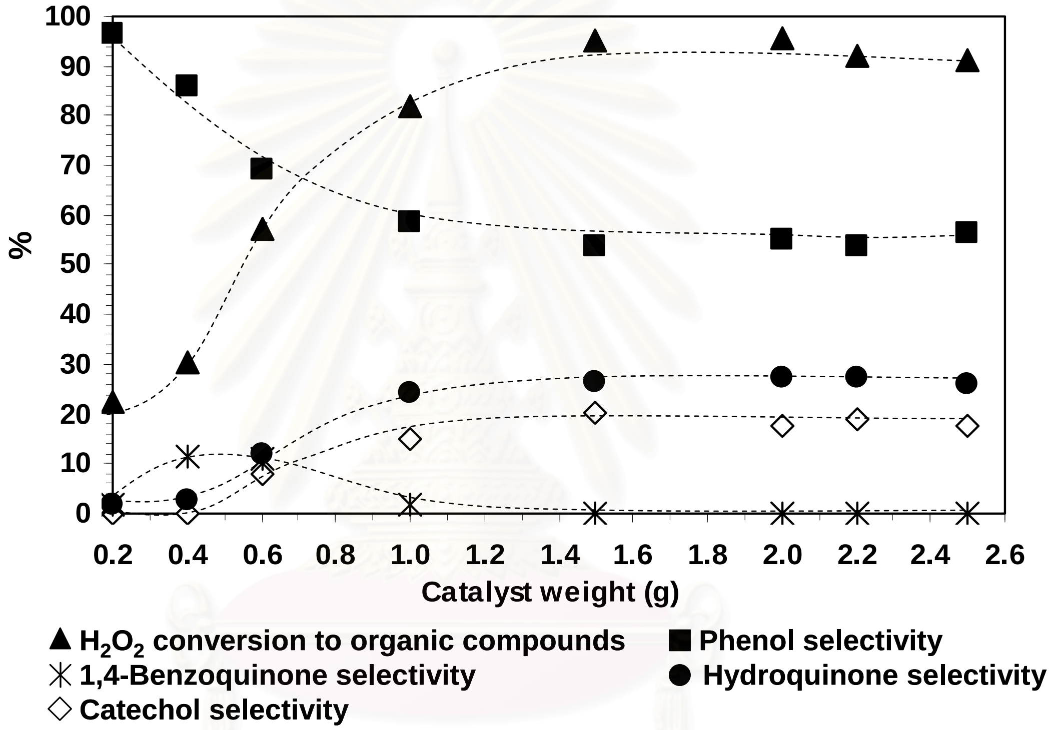


Figure 4.24 H_2O_2 conversion to organic compounds and product selectivity as a function of catalyst weight in the selective oxidation of benzene catalyzed by TS-PQ^{TM}. Reaction conditions: atmospheric pressure, temperature 70°C, 0.011 mole of H_2O_2 and 0.056 mole of benzene, 40 ml additional water, stirring speed 1100 rpm, reaction time 3 h.

Iodometry and permanganate titration were applied to confirm the decomposition of H_2O_2. In the absence of catalyst and benzene, keeping the mixture temperature at 70°C for 3 h, the observed H_2O_2 decomposition was approximately

2%. In the presence of catalyst and benzene, only iodometry titration can be applied due to the interference of organics in the mixture.

In the presence of 1.5 g or 2.5 g catalyst and benzene under reaction conditions mentioned in **Figure 4.24**, the total conversion of H_2O_2 including decomposition analyzed by mean of iodometry was found to be around 96-97%. That percentage is higher than the conversion of H_2O_2 to organic compounds calculated from equation **(3.7)** around 1-2%. These differences definitely come from the decomposition of H_2O_2 by heat or other factors such as light exposure or stirring speed which we did not consider it in equation **(3.7)**. The value is also in good agreement with the study of H_2O_2 decomposition in the absence of catalyst and benzene as mentioned before. Therefore, at around 95% of the initial H_2O_2 was converted to the desired products. Approximately 2% were decomposed and around 3% of initial H_2O_2 was unused for the reaction which might be considered to be due to the excessive dilution of H_2O_2 in the mixture.

In addition, from the material balance cited above, the possibility of tar formation via oxygenated products was only to a minor extent. After the reaction the catalyst had a light pale brown color indicating only negligible tar formation.

4.2.2.6 The effect of reaction time on the conversion of H_2O_2 to organic compounds and product selectivity

Figure 4.25 exhibits H_2O_2 conversion to organic compounds and product selectivity as a function of reaction time. The H_2O_2 conversion increased gradually when the reaction time increased from 0.5 h to 3 h and remained stable at around 95% after 3 h. The phenol selectivity decreased while selectivity of minor products, hydroquinone and catechol, increased at longer reaction time. After 3 h, phenol product remained at 54% selectivity followed by hydroquinone at 26% and catechol 20% selectivity. It is in accordance with the study of H_2O_2 decomposition and the effect of catalyst weight that H_2O_2 can reach highest value at around 95% even leaving the reaction in longer time could not make a significant change of conversion and product selectivity.

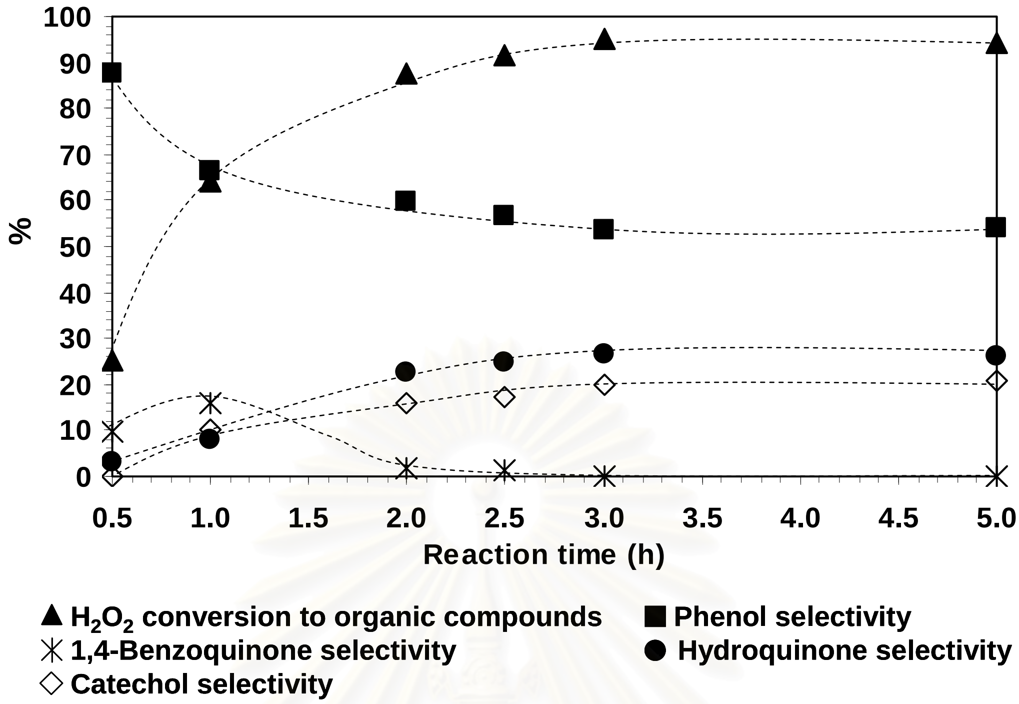


Figure 4.25 H_2O_2 conversion to organic compounds and product selectivity as a function of reaction time in the selective oxidation of benzene catalyzed by TS-PQ^{TM}. Reaction conditions: atmospheric pressure, temperature 70°C, 0.011 mole of H_2O_2 and 0.056 mole of benzene, 40 ml additional water, stirring speed 1100 rpm, catalyst 1.5 g.

The stability of TS-PQ^{TM} catalyst was investigated by using the catalyst several times with and without washing the catalyst using acetone before the next run. If the catalyst, filtered after the reaction, was used again as it was, H_2O_2 conversion was almost the same as the fresh catalyst. The activity started dropping approximately 30% of the fresh catalyst in the third recycling step. In contrary washing the catalyst with acetone after each usage helped maintaining its activity. Then, the catalyst can be used without loss in activity for more than three times of reuse. This result can also indicated that almost no tar or only small amounts were formed in the first run as well as the leaching of Ti active sites could not be observed by hot filtration test [Wagner *et al.*, 2001].

CHAPTER V

CONCLUSION AND RECOMENDATION

5.1 Conclusion

The catalytic performance of TS-PQ^{TM} is superior over synthesized TS-1 and Ti-MCM-41 in the selective oxidation of benzene using H_2O_2 as oxidant to form phenol. For typical TS-1 catalyst containing only isolated tetrahedral Ti^{4+} atoms, the use of solvent is believed to affect the catalytic process by stabilizing Ti^{4+} and generating lattice defects as an active site for the reaction. In contrast, titanium silicate catalyst, which is already distorted by non-isolated substituted titanium like TS-PQ^{TM}, does not need any solvent and shows a superior catalytic property in solvent free system even though TS-PQ^{TM} catalyst in this study has less titanium content than TS-1. In combination with other differences in the physical features such as higher hydrophilicity, higher surface area, higher pore volume as well as larger mesopores of TS-PQ^{TM} resulting in reduced diffusion hindrance, it is the most preferable for three phase systems. The effects of pressure, H_2O_2 addition rate, stirring speed, reaction temperature, benzene/H_2O_2 molar ratio, volume of additional water, catalyst amount and reaction time were studied. Vigorous mixing is needed in the three phase slurry reactor system in order to increase the opportunity of the substrates to encounter active sites. Appropriate reaction temperature for this study was found to be at 70°C. Additional water plays a role by improving the catalyst suspension in the mixture and stripping phenol from the active sites. The catalyst amount and reaction time have a strong influence on the H_2O_2 and product selectivity based on the overall produced products. Under mild conditions, such as 70°C and atmospheric pressure, TS-PQ^{TM} exhibited around 20% H_2O_2 conversion to organic compounds with excellent phenol selectivity, more than 90%. Around 95% of H_2O_2 conversion to produce phenol and other valuable products could be obtained by increasing the amount of catalyst as well as reaction time which achieves the desirable target in this one-step process.

5.2 Recommendation

TS-PQ^{TM} catalyst exhibits excellent performance in the selective oxidation of benzene to produce phenol. It is worthwhile to use this catalyst under the studied conditions to produce phenol from benzene in one step process instead of three-step process, cumene route. Therefore, the process needs to be scaled up in particular higher amount of substrate should be added or CSTR reactor should be applied.

Due to the fact that the reaction needs a vigorous mixing, therefore, type of stirring should have effect to the reaction. Higher conversion and selectivity should be obtained under appropriate amount of substrate in combination with the sufficient of vigorous mixing.

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APPENDICES

APPENDIX A

GC STANDARD PREPARARTION AND CALIBRATION CURVES FOR PRODUCT ANALYSIS

This part demonstrates the calculation of standard sample preparation and calibration curves. Gas chromatograph equipped with flame ionization detector was used to analyze the quantity of reaction products. Either molar concentration basis or weight percent basis can be used for the calculation of standard sample concentration.

The standard samples of the products (phenol, catechol, hydroquinone and 1,4-benzoquinone) were prepared in a 10 ml volumetric flask. The chemical standard in solid phase was weighted into the flask with a 4 decimals digital balance. Ethanol was filled into the volumetric flask until the level of solution reached 10 ml mark line. The sample was weighted again and the overall weight of the sample was calculated.

The concentration of standard samples was calculated based on weight percent basis and molar basis using the equations below;

Weight percent basis

$$\text{Concentration of standard i (w/w \%)} = \left(\frac{w_i}{W} \times 100\right) \qquad \textbf{(1A)}$$

Molar basis

$$\text{Concentration of standard i } (M_i) = \left(\frac{w_i}{M.W._i \times V}\right) \qquad \textbf{(2A)}$$

Where;

w_i	is weight of standard i in the sample in gram
$M.W._i$	is the molecular weight of standard i in gram per mole
V	is the volume of sample in liter (in this case equal to 0.01 l)
W	is the total weight of sample

Different concentrations of standard samples were prepared. The relation between concentration of standard sample and peak area from integrator is plotted. For the weight percent basis, concentration (w/w %) of the standards are plotted in y axis and peak area from integrator are plotted in x axis as showed in **Figures 1A** to **4A**.

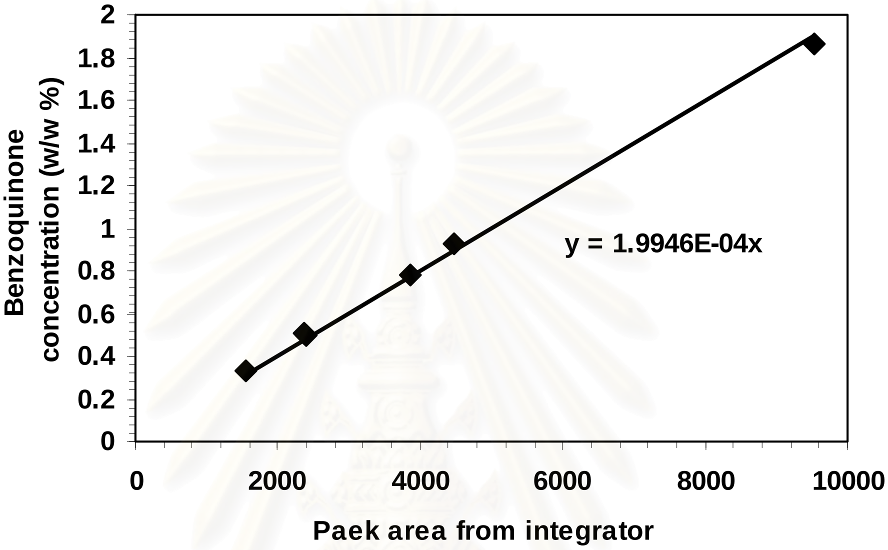

Figure 1A The calibration curve of 1,4-Benzoquinone from gas chromatograph HP 7890 equipped with capillary column CP-SIL8.

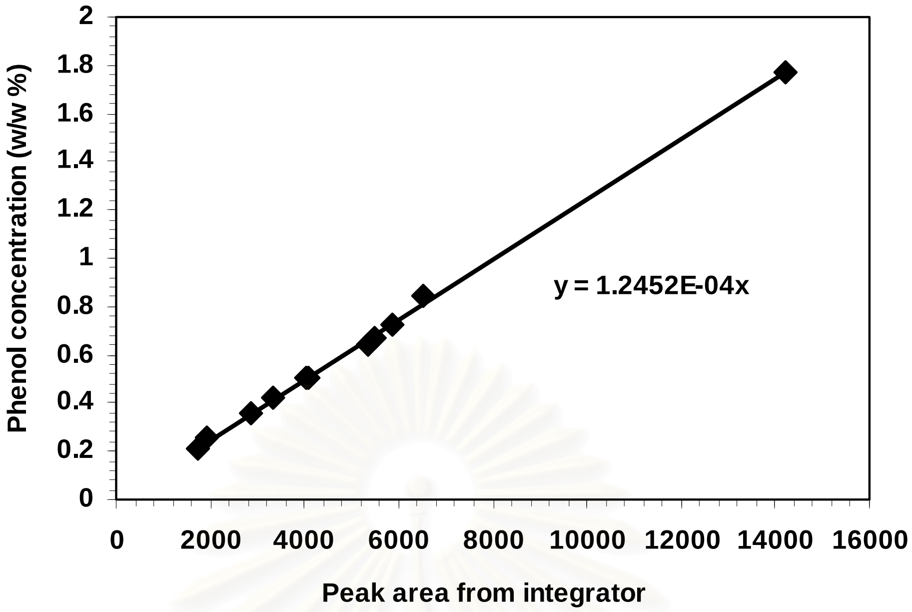

Figure 2A The calibration curve of phenol from gas chromatograph HP 7890 equipped with capillary column CP-SIL8.

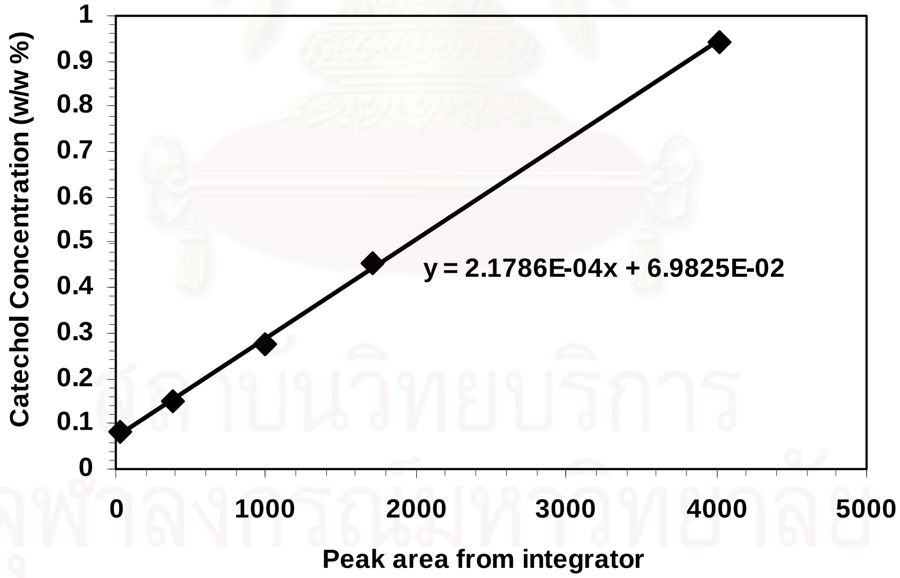

Figure 3A The calibration curve of catechol from gas chromatograph HP 7890 equipped with capillary column CP-SIL8.

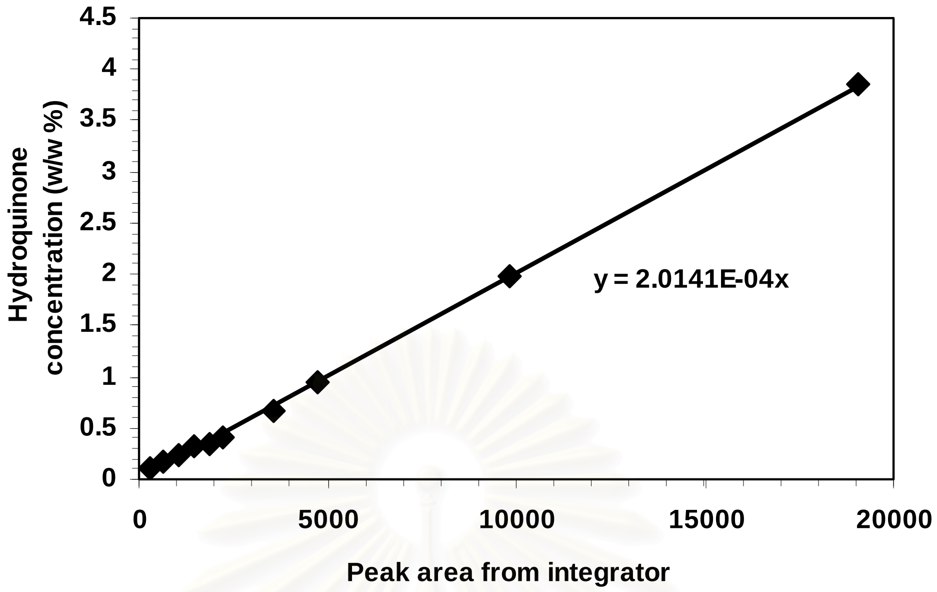

Figure 4A The calibration curve of hydroquinone from gas chromatograph HP 7890 equipped with capillary column CP-SIL8.

For the molar basis calculation, mole of standard was calculated according to the injected volume of sample to gas chromatography. In the case of GC system with split injection system, it is necessary to use the split ratio value to calculate the real volume of sample which has been injected to GC (e.g. the standard is injected 1 μl with the split ratio condition 9:1, it means that only 1 portion of sample is injected and 9 portion of sample is discarded). Mole of standard calculation is shown in equation below;

$$m_i = M_i \times v_{inj} \qquad \textbf{(3A)}$$

Where;

m_i is mole of standard i

M_i is the molar concentration of standard i

v_{inj} is the injection volume of sample to gas chromatography

The calibration curves showing the relation between mole of products in y axis and peak areas from integrator in x axis are showed in **Figures 5A** to **12A**.

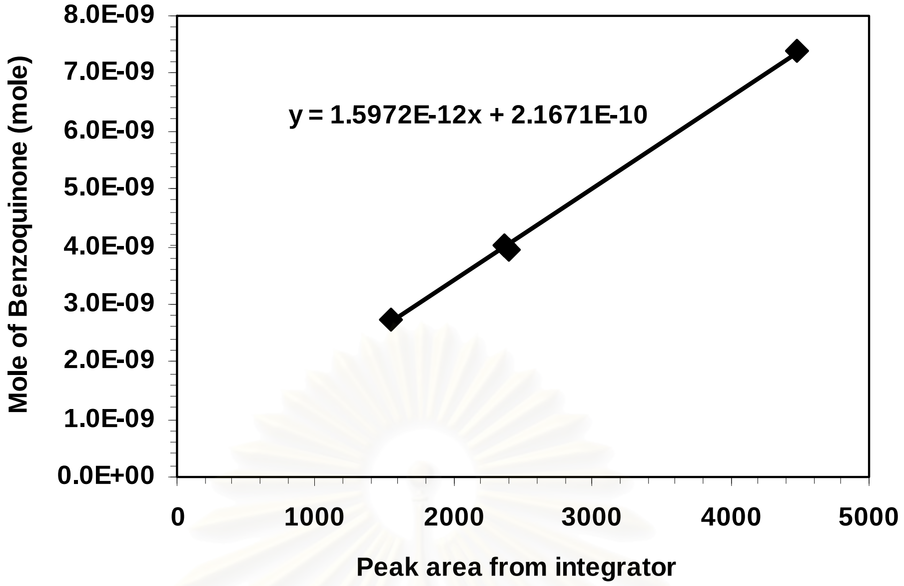

Figure 5A The calibration curve of 1,4-Benzoquinone from gas chromatograph HP 7890 equipped with capillary column CP-SIL8.

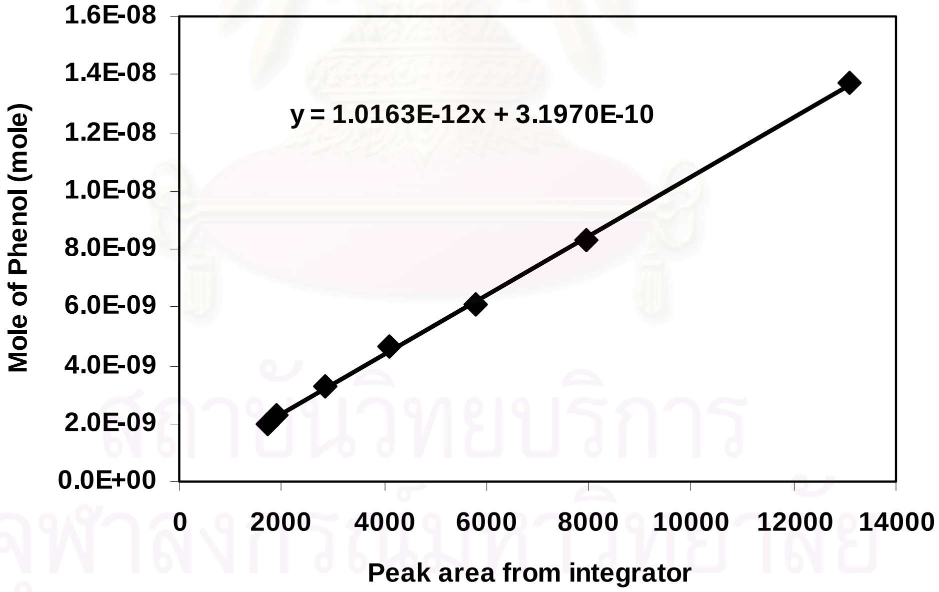

Figure 6A The calibration curve of phenol from gas chromatograph HP 7890 equipped with capillary column CP-SIL8.

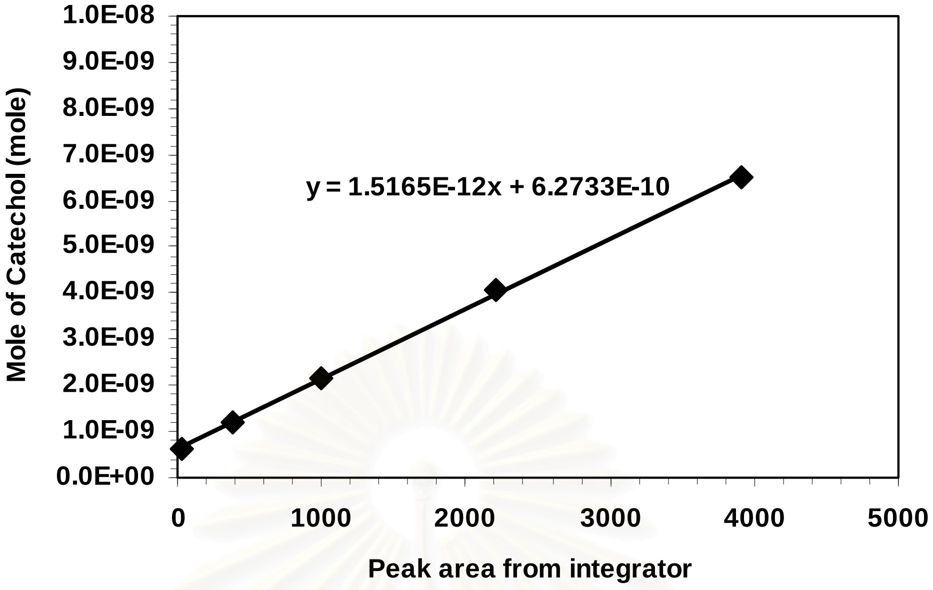

Figure 7A The calibration curve of catechol from gas chromatograph HP 7890 equipped with capillary column CP-SIL8.

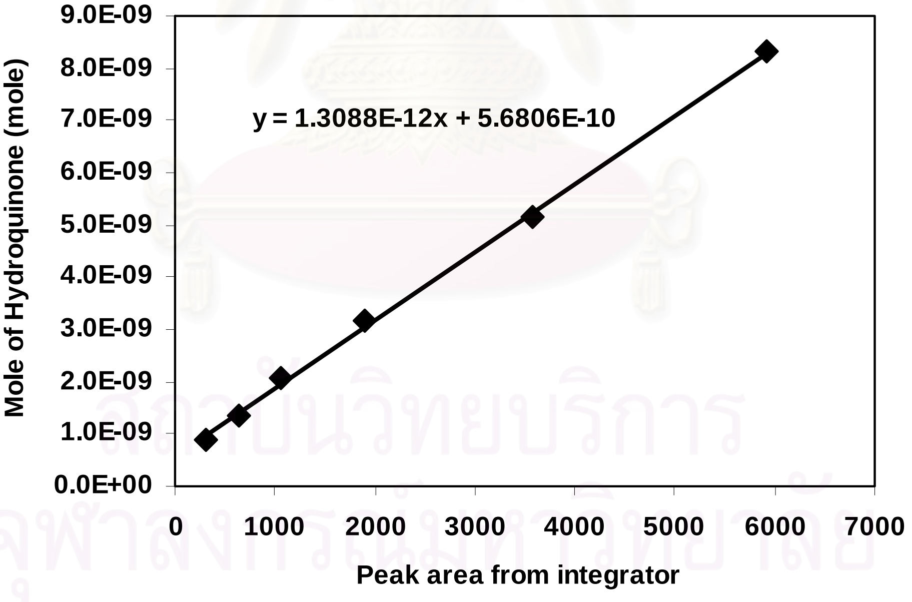

Figure 8A The calibration curve of hydroquinone from gas chromatograph HP 7890 equipped with capillary column CP-SIL8.

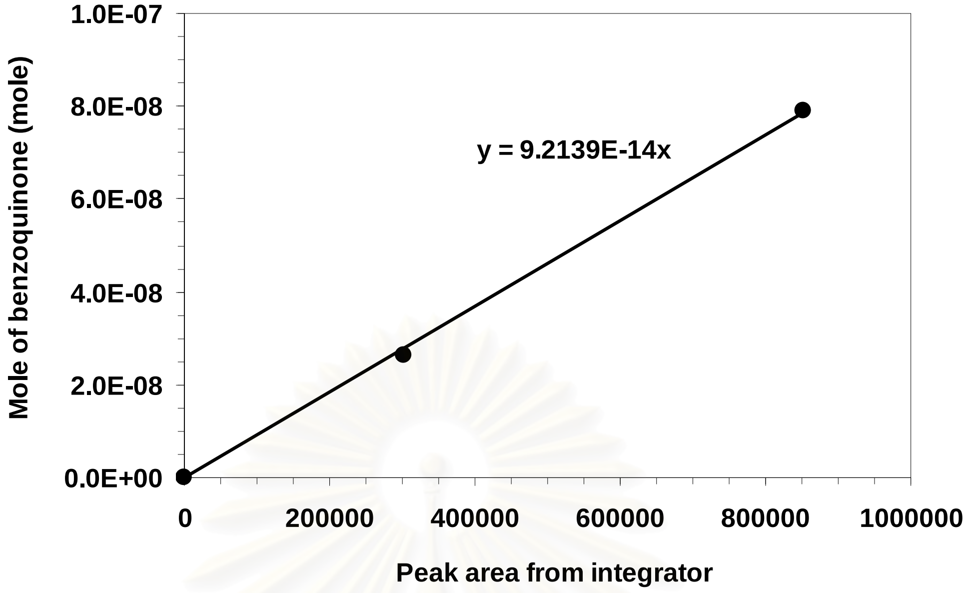

Figure 9A The calibration curve of 1,4-benzoquinone from gas chromatograph Shimadzu 9A equipped with packed column GP 10% SP-2100.

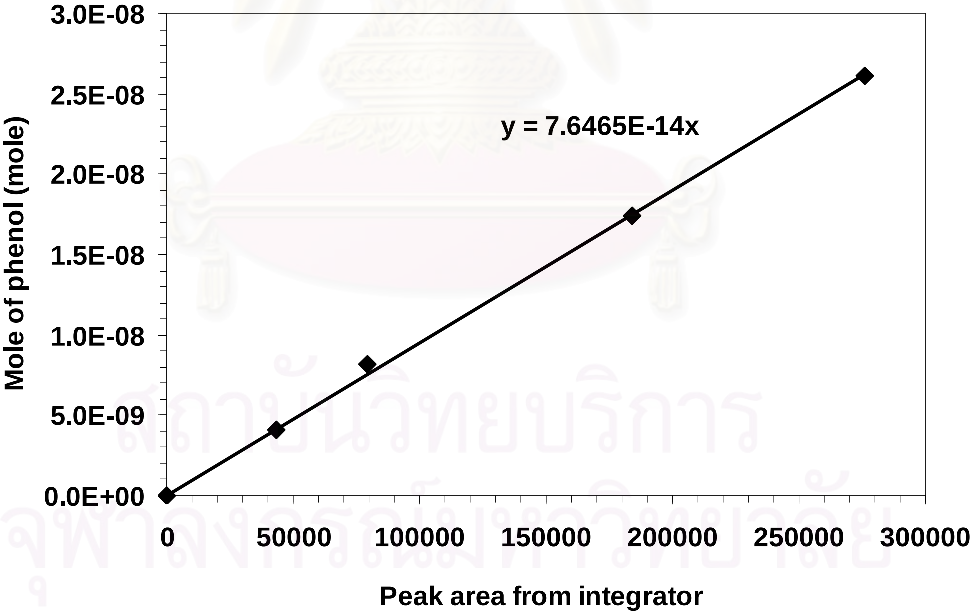

Figure 10A The calibration curve of phenol from gas chromatograph Shimadzu 9A equipped with packed column GP 10% SP-2100.

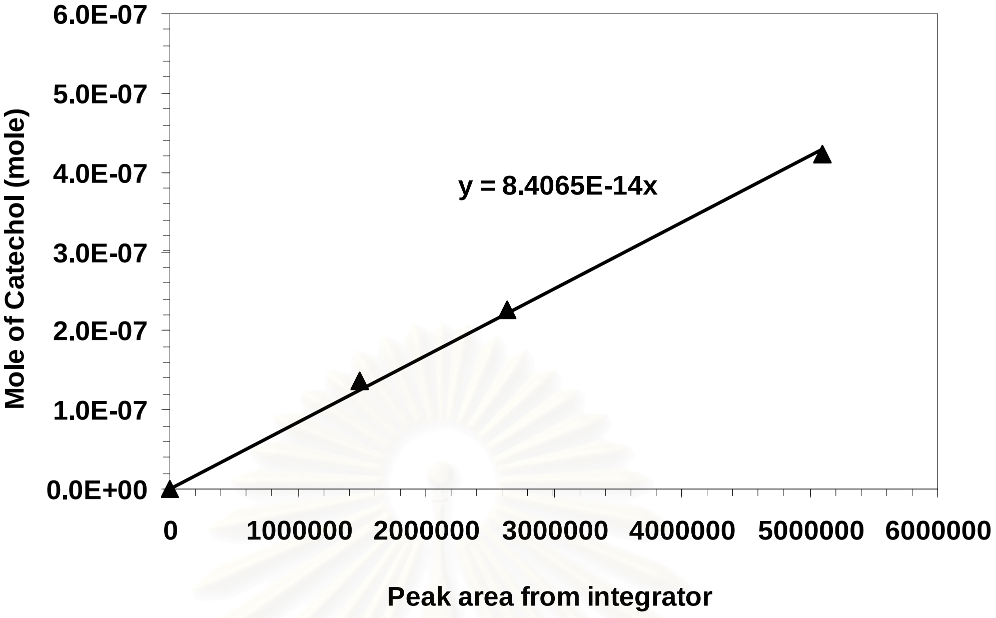

Figure 11A The calibration curve of catechol from gas chromatograph Shimadzu 9A equipped with packed column GP 10% SP-2100.

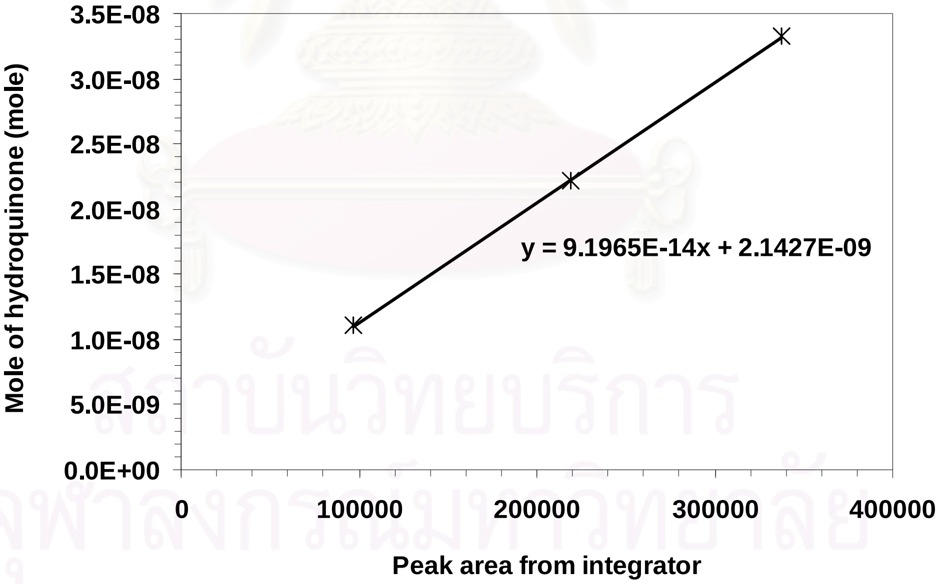

Figure 12A The calibration curve of hydroquinone from gas chromatograph Shimadzu 9A equipped with packed column GP 10% SP-2100.

APPENDIX B

EXAMPLE OF CONVERSION AND PRODUCT SELECTIVITY CALCULATION

Appendix B describes the calculation of conversion and product selectivity by using equations from chapter III. After the reaction, ethanol or methanol was used to homogenize the mixture before injecting the small portion of sample to GC. The peak areas of the reaction products related to phenol, 1,4-benzoquinone, hydroquinone and catechol were transformed to weight percent basis or molar basis of product in sample using slope from the correlated calibration curve. The concentration of GC sample was then multiplied with the total weight or volume of sample to obtain the overall amount of product.

In weight percent basis, the overall mole of each product was calculated by multiplying its concentration with the total weight of the sample after homogenizing with solvent and divided by molecular weight as follows;

$$n_i = \left(\frac{A_i \times \mathrm{Slope}_i \times W}{\mathrm{M.W.}_i} \right) \qquad \textbf{(1B)}$$

Where ;

n_i is the overall mole of product i in the sample (product i, are phenol, catechol, 1,4- benzoquinone and hydroquinone)

A_i is the peak area of product i

Slope_i is the slope from the correlated calibration curve

W is the total weight of sample (after homogenizing with solvent)

In molar percent basis, the overall mole of each product was calculated following equation **(2B)** below;

$$n_i = \left(\frac{A_i \times \mathrm{Slope}_i \times V}{v_{inj}} \right) \qquad \textbf{(2B)}$$

Where ;

n_i	is the overall mole of product i in the sample
A_i	is the peak area of product i
$Slope_i$	is the slope from the correlated calibration curve
V	is the total volume of sample (after homogenizing with solvent)
v_{inj}	is the injection volume of sample to gas chromatography

The examples of the calculation used weight percent basis and molar basis are shown below;

Reaction conditions; 1.5 g of TS-PQ^{TM} catalyst, benzene 5.6329 $\times10^{-2}$ mole, H_2O_2 (30 wt.%) 1.3229$\times10^{-2}$ mole, reaction temperature 70°C under atmospheric pressure, reaction time 3 h with stirring speed 1100 rpm.

After 3 h, the reaction was stopped by placing the reactor into ice bath. Ethanol was mixed to the sample and stirred to obtain the homogeneous phase. The total weight of final mixture was 87.5132 g and the total volume was 100 ml. The catalyst particle was separated by using centrifuge. 1 μl of sample was injected to GC (HP 7890 equipped with capillary column CP-SIL8, split ratio 8.2:1). Mole of H_2O_2 left after reaction analyzing by iodometric titration was 5.0585$\times10^{-4}$ mole. The peak areas of products are listed below;

Product	**Peak area**
1,4-Benzoquinone	0
Phenol	3317.3462
Catechol	512.9553
Hydroquinone	827.8834

Under above conditions, three products were observed. The overall moles of each product calculated based on weight percent basis from equation **(1B)** and molar basis from equation **(2B)** are in following;

Weight percent basis;

$$n_{\text{Phenol}} = \left(\frac{3317.3462 \times 1.2452 \times 10^{-4} \times 87.5132}{100 \times 94.11}\right)$$

$$n_{\text{Phenol}} = 3.8412 \times 10^{-3} \text{ mole}$$

$$n_{\text{Catechol}} = \left(\frac{\left((512.9553 \times 2.1746 \times 10^{-4}) + (7.1189 \times 10^{-2})\right) \times 87.5132}{100 \times 110.1}\right)$$

$$n_{\text{Catechol}} = 1.4524 \times 10^{-3} \text{ mole}$$

$$n_{\text{Hydroquinone}} = \left(\frac{827.8834 \times 2.0141 \times 10^{-4} \times 87.5132}{100 \times 110.1}\right)$$

$$n_{\text{Hydroquinone}} = 1.3253 \times 10^{-3} \text{ mole}$$

The total H_2O_2 conversion calculated from equation **(3.8)** and the H_2O_2 conversion to organic compounds calculated from equation **(3.7)** are;

$$C_{H_2O_2} = \left(\frac{\left(1.3229 \times 10^{-2}\right) - \left(5.0585 \times 10^{-4}\right)}{1.3229 \times 10^{-2}}\right) \times 100$$

$$C_{H_2O_2} = 96.17\,\%$$

$$C_{H_2O_2,\,\text{Org.}} = \frac{(3.8412 \times 10^{-3}) + (2 \times 1.4524 \times 10^{-3}) + (2 \times 1.3253 \times 10^{-3})}{1.3229 \times 10^{-2}} \times 100$$

$$C_{H_2O_2,\,\text{Org.}} = 71.03\,\%$$

Molar basis;

$$n_{\text{Phenol}} = \left(\frac{\left(\left(3317.3462 \times 1.0163 \times 10^{-12}\right) + \left(3.1970 \times 10^{-10}\right)\right) \times \left(100\ \text{ml} \times \dfrac{10^{-3}\ \text{l}}{1\,\text{ml}}\right)}{\left(1\,\mu\text{l} \times \dfrac{10^{-6}\ \text{l}}{1\,\mu\text{l}}\right) \times \left(\dfrac{1}{9.2}\right)} \right)$$

$$n_{\text{Phenol}} = 3.3958 \times 10^{-3}\ \text{mol}$$

$$n_{\text{Catechol}} = \left(\frac{\left(\left(512.9553 \times 1.5165 \times 10^{-12}\right) + \left(6.2733 \times 10^{-10}\right)\right) \times \left(100\ \text{ml} \times \dfrac{10^{-3}\ \text{l}}{1\,\text{ml}}\right)}{\left(1\,\mu\text{l} \times \dfrac{10^{-6}\ \text{l}}{1\,\mu\text{l}}\right) \times \left(\dfrac{1}{9.2}\right)} \right)$$

$$n_{\text{Catechol}} = 1.2928 \times 10^{-3}\ \text{mol}$$

$$n_{\text{Hydroquinone}} = \left(\frac{\left(\left(827.8834 \times 1.3088 \times 10^{-12}\right) + \left(5.6806 \times 10^{-10}\right)\right) \times \left(100\ \text{ml} \times \dfrac{10^{-3}\ \text{l}}{1\,\text{ml}}\right)}{\left(1\,\mu\text{l} \times \dfrac{10^{-6}\ \text{l}}{1\,\mu\text{l}}\right) \times \left(\dfrac{1}{9.2}\right)} \right)$$

$$n_{\text{Hydroquinone}} = 1.5195 \times 10^{-3}\ \text{mol}$$

$$C_{\text{H}_2\text{O}_2,\,\text{Org.}} = \left(\frac{(3.3958 \times 10^{-3}) + (2 \times 1.2928 \times 10^{-3}) + (2 \times 1.5195 \times 10^{-3})}{1.3229 \times 10^{-2}} \right) \times 100$$

$$C_{\text{H}_2\text{O}_2,\,\text{Org.}} = 68.18\,\%$$

The conversions calculated from weight percent basis and molar basis as the example above are similar. To minimize the error of volume measurement from eye-measuring, the calculation based on weight percent is preferable. The product selectivity is further calculated using equations **(3.10)**, **(3.12)** and **(3.13)** as shown below;

$$S_{Phenol} = \frac{3.8412\times10^{-3}}{(3.8412\times10^{-3})+(1.4524\times10^{-3})+(1.3253\times10^{-3})}\times100$$

$$S_{Phenol} = 58.03\,\%$$

$$S_{Catechol} = \frac{1.4524\times10^{-3}}{(3.8412\times10^{-3})+(1.4524\times10^{-3})+(1.3253\times10^{-3})}\times100$$

$$S_{Catechol} = 21.94\,\%$$

$$S_{Hydroquinone} = \frac{1.3253\times10^{-3}}{(3.8412\times10^{-3})+(1.4524\times10^{-3})+(1.3253\times10^{-3})}\times100$$

$$S_{Hydroquinone} = 20.02\,\%$$

APPENDIX C

CALCULATION OF THE REQUIRED AMOUNT OF SOLVENT FOR HOMOGENIZING THE MIXTURE

In multiple phase reaction, the analysis of product could be done in many ways such as analyzing the product in each phase separately, to use the solvent to extract product from the mixture and to homogenize the mixture with solvent. In this research, ethanol or methanol was used to homogenize the mixture before GC analysis. The insufficient of solvent can lead to analysis error. Therefore, the required amount of solvent was calculated by using triangular phase diagram. The triangular phase diagram of ethanol-benzene-water system as showed in **Figure 1C**.

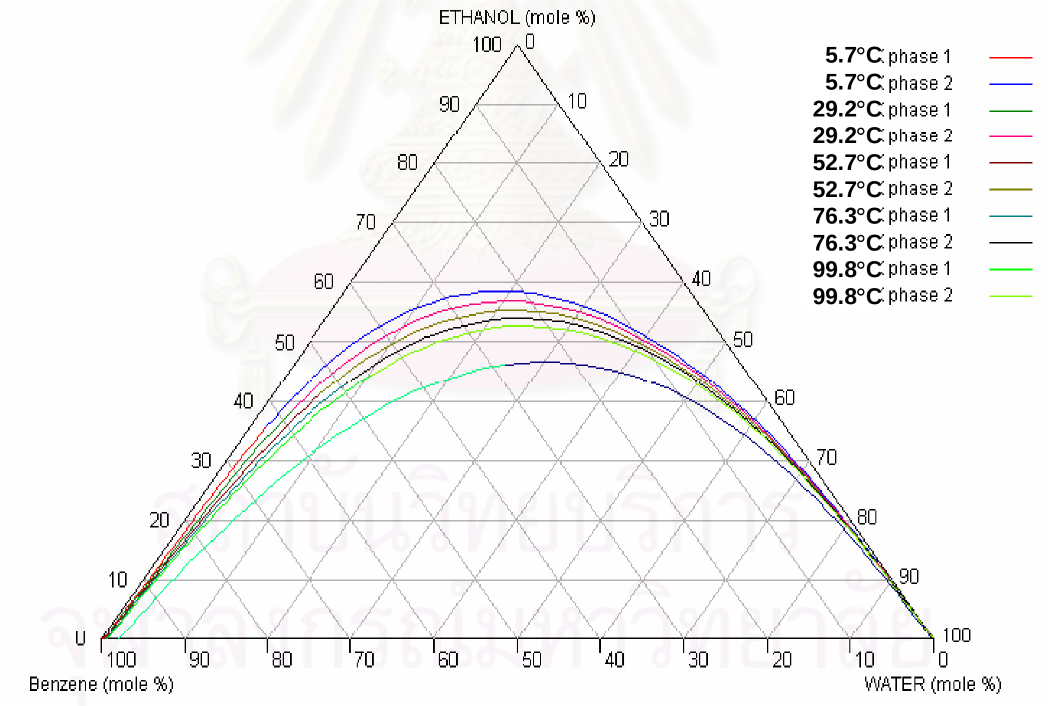

Figure 1C Triangular phase diagram for ethanol-benzene-water system [Sales-Curz, 2004].

In the triangular phase diagram, the corner of the triangle represents 100% of the corresponding component. Therefore, pure benzene, ethanol and water exist at the top corner. The mixture containing two components lie on an edge of the triangle. All points of straight line between benzene and water edge through the corner of ethanol represent the same ratio of benzene and water while ethanol is added to the mixture. The region below the curve shows two phase mixture. All fractions above the curve exhibit homogeneous phase of three substrates.

For the experiment in this research, the estimation of benzene and water mole fractions was done. Any point above the curve on the straight line lies from benzene-water mole fraction in the mixture through the corner of ethanol could be used as the required amount of ethanol to homogenize the mixture. The calculation example for the following reaction conditions is shown below;

Reaction condition; Benzene 5 ml (0.056 mole)
H_2O_2 (30 wt.%) 1.14 ml (0.0112 mole H_2O_2)
Additional water 40 ml

The experiment was initially assumed that H_2O_2 conversion was 100%, the content of water from the H_2O_2 aqueous solution after reaction was calculated around 0.9 g and water produced from the reaction was calculated around 0.2 g (0.0112 mole). The overall content of water and benzene in the mixture after reaction are in following;

H_2O from H_2O_2 solution + H_2O from the reaction + additional H_2O = 41.1 g
= 2.28 mole
Benzene left after reaction = 0.0448 mole
The content of water in the mixture after reaction = 98 mol%
The content of benzene in the mixture after reaction = 2 mol%

The straight line from the estimation point (98 mol% water and 2 mol% benzene) to the corner of ethanol is drawn **Figure 2C**.

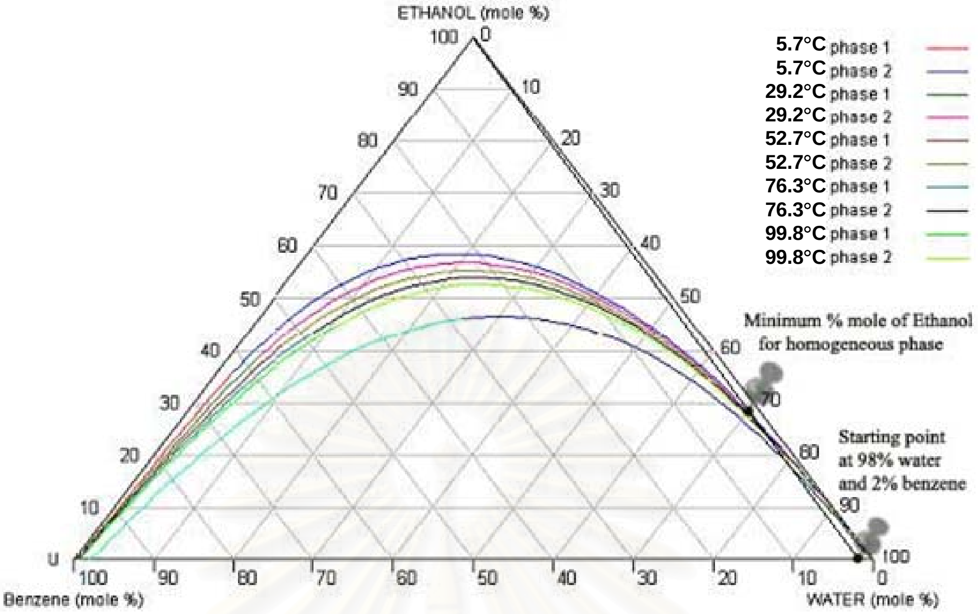

Figure 2C Estimation the required amount of ethanol.

From **Figure 2C**, the minimum required amount of ethanol is 30 mol%, approximately. At this point, the content of benzene and water are around 1.4 and 68.6 mol%, respectively. Therefore, the minimum required amount of ethanol is;

$$\frac{2.28\,\text{mole H}_2\text{O}\times 30\,\%\,\text{EtOH}}{68.6\,\%\,\text{H}_2\text{O}} = 0.9971\,\text{mole EtOH}\ \ (45.87\text{ g})$$

APPENDIX D

DATA OF EXPERIMENTS

Table 1D The effect of molar ratio between benzene/H_2O_2 on the H_2O_2 conversion to organic compounds and product selectivity.

Molar ratio	$C_{H_2O_2,\,Org.}$ (%)	S_{Phenol} (%)	$S_{1,4\text{-}Benzoquinone}$ (%)	$S_{Catechol}$ (%)	$S_{Hydroquinone}$ (%)
1:1	7.37	89.20	8.10	0	2.69
3:1	15.52	86.67	11.44	0.02	1.87
5:1	19.35	92.42	6.25	0	1.33
7:1	16.95	92.96	4.55	0	2.49
10:1	19.21	92.03	6.17	0.02	1.78

Table 2D The effect of additional water on the H_2O_2 conversion to organic compounds and product selectivity.

Additional water (ml)	$C_{H_2O_2,\,Org.}$ (%)	S_{Phenol} (%)	$S_{1,4\text{-}Benzoquinone}$ (%)	$S_{Catechol}$ (%)	$S_{Hydroquinone}$ (%)
0	9.60	65.64	30.94	0.04	3.37
10	15.97	82.01	16.48	0	1.51
15	16.42	87.67	9.86	0.01	2.45
20	19.35	92.42	6.25	0	1.33
30	21.03	93.15	4.40	0	2.45
40	22.54	96.35	1.77	0.03	1.85
50	19.79	94.75	0.02	0.03	5.20
60	18.70	98.18	0.01	0.02	1.79

Table 3D The effect of amount of catalyst on the conversion and product selectivity.

Catalyst amount (g)	**$C_{H_2O_2,\ Org.}$ (%)**	**S_{Phenol} (%)**	**$S_{1,4\text{-}Benzoquinone}$ (%)**	**$S_{Catechol}$ (%)**	**$S_{Hydroquinone}$ (%)**
0.2	22.54	96.35	1.77	0.03	1.85
0.4	30.38	85.83	11.62	0	2.55
0.6	57.25	69.04	11.02	8.01	11.93
1.0	81.81	58.75	1.80	15.16	24.29
1.1	85.46	58.75	1.54	14.49	25.23
1.3	86.44	57.62	1.48	16.02	24.88
1.5	95.12	53.61	0	20.05	26.34
2.0	95.71	55.08	0	17.66	27.26
2.2	91.94	53.65	0	18.92	27.43
2.5	91.10	56.55	0	17.44	26.01

Table 4D The effect of reaction time on the conversion and product selectivity

Reaction time (h)	**$C_{H_2O_2,\ Org.}$ (%)**	**S_{Phenol} (%)**	**$S_{1,4\text{-}Benzoquinone}$ (%)**	**$S_{Catechol}$ (%)**	**$S_{Hydroquinone}$ (%)**
0.5	25.26	87.47	9.52	0.10	2.91
1	64.24	66.20	15.72	10.20	7.88
2	87.54	59.56	1.78	15.94	22.73
2.5	91.41	56.79	1.16	17.10	24.94
3	95.12	53.61	0	20.05	26.34
5	94.20	54.01	0	20.97	25.02

APPENDIX E

MATERIAL SAFETY DATA SHEET OF BENZENE, HYDROGEN PEROXIDE AND REACTION PRODUCTS

Safety data for benzene

General

Synonyms: benzol, phenyl hydride, coal naphtha
Molecular formula: C_6H_6

Physical data

Appearance : colourless liquid
Melting point : 5.5°C
Boiling point : 80°C
Specific gravity : 0.87
Vapour pressure : 74.6 mm Hg at 20 °C
Flash point : -11 °C
Explosion limits : 1.3 % - 8 %
Autoignition temperature: 561 °C

Stability

Stable. Substances to be avoided include strong oxidizing agents, sulfuric 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.

Safety data for phenol

General

Synonyms: benzenol, carbolic acid, hydroxybenzene, monohydroxybenzene, monophenol, oxybenzene, phenic acid, phenylic acid, phenyl alcohol, phenyl hydrate, phenyl hydroxide, phenylic alcohol
Molecular formula: C_6H_5OH

Physical data

Appearance : colourless crystals with a characteristic odour
Melting point : 40°C -42°C
Boiling point : 182°C
Specific gravity : 1.07
Vapour pressure : 0.35 mm Hg at 20°C
Flash point : 79°C
Explosion limits : 1.5 % - 8.6 %
Autoignition temperature: 715°C

Stability

Stable. Substances to be avoided include strong oxidizing agents, strong bases, strong acids, alkalies, calcium hypochlorite. Flammable. May discolour in light.

Toxicity

This material is a systemic poison and constitutes a serious health hazard. The risks of using it in the laboratory must be fully assessed before work begins. Vesicant. Typical MEL 2 ppm; typical OEL 1 ppm. Acute poisoning by ingestion, inhalation or skin contact may lead to death. Phenol is readily absorbed through the skin. Highly toxic by inhalation. Corrosive - causes burns. Severe irritant.

Personal protection

Safety glasses, gloves, good ventilation.

Safety data for 1,4 Benzoquinone

General

Synonyms: benzoquinone, p-benzoquinone, cyclohexadienedione, 1,4-cyclohexadienedione, 2,5-cyclohexadiene-1,4-dione, 1,4-dioxybenzene, quinone.
Molecular formula: $C_6H_4O_2$

Physical data

Appearance : gold powder
Melting point : 113-115°C
Boiling point : ca. 180°C
Vapour pressure : 0.1 mm Hg at 25°C
Autoignition temperature: 560°C

Stability

Stable but light sensitive. Incompatible with strong oxidizing agents. Flammable.

Toxicology

Toxic. May be fatal if swallowed, inhaled or absorbed through skin. Severe irritant.

Personal protection

Safety glasses, gloves. Effective ventilation.

Safety data for catechol

General

Synonyms: o-dihydroxybenzene, o-benzenediol, 1,2-benzenediol, catechin, 1,2-dihydroxybenzene, o-hydroxyphenol, 2-hydroxyphenol, oxyphenic acid, phthalhydroquinone, C.I. 76500, C.I. oxidation base 26, pelagol grey c, pyrocatechin

Molecular formula: $C_6H_6O_2$

Physical data

Appearance	: white to tan solid
Melting point	: 104-106°C
Boiling point	: 245°C
Vapour pressure	: 1 mm Hg at 75°C
Vapour density	: 3.8
Flash point	: 137°C
Explosion limits	: 1.97% (lower)

Stability

Stable. Substances to be avoided include acid chlorides, acid anhydrides, bases, oxidizing agents, nitric acid. Light sensitive; may discolour on exposure to air. Combustible.

Toxicology

Corrosive, causes burns. Harmful by inhalation, ingestion and through skin absorption. Readily absorbed through skin. Very destructive of mucous membranes and upper respiratory tract, eyes and skin. Target organs: CNS, kidneys, liver.

Personal protection

Safety glasses. Suitable ventilation.

Safety data for hydroquinone

General

Synonyms: alpha-hydroquinone, hydroquinol, quinol, benzoquinol, p-benzenediol, 1,4-benzenediol, p-dihydroxybenzene, p-hydroxyphenol, p-dioxobenzene, 1,4-dihydroxybenzene, dihydroquinone, pyrogentistic acid, quinnone, aida, arctuvin, eldoquin, eldopaque, phiaquin, tecquinol, tenox HQ, tequinol
Molecular formula: $C_6H_6O_2$

Physical data

Appearance : off-white powder or white needle-like crystals
Melting point : 172-175°C
Boiling point : 285°C
Vapour density : 3.81 (air = 1)
Vapour pressure : 1 mm Hg at 132°C
Density (g cm^{-3}) : 1.33
Flash point : 165°C
Autoignition temperature: 498°C
Water solubility : moderate

Stability

Stable. Combustible. Incompatible with strong oxidizing agents, strong bases, oxygen, ferric salts. Light and air-sensitive. Discolours in air.

Toxicology

Possible carcinogen. Severe skin irritant; allergen. Harmful by inhalation and ingestion. May cause sensitization. Eye and respiratory irritant.

Personal protection

Safety glasses, gloves, adequate ventilation. Treat as a potential carcinogen.

Safety data for hydrogen peroxide, 30% solution

General

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

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

Physical data

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

Stability

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

Toxicology

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

Personal protection

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

APPENDIX F

LIST OF PUBLICATION

Chammingkwan, P., Hoelderich, W. F., Mongkhonsi, T.’ Kanchanawanichakul, P. Hydroxylation of benzene over TS-PQ^{TM} catalyst. **Applied catalysis A: General** (manuscript is accepted).

VITA

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