โครงการ
การเรียนการสอนเพื่อเสริมประสบการณ์

ชื่อโครงการ ฟิล์มบางรูพรุนไทเทโนซิลิเกตบนเส้นลวดนาโนซิลิกอนเพื่อเป็นตัวเร่งปฏิกิริยาออกซิเดชัน
Titanosilicate porous thin film on silicon nanowire as catalyst for oxidation

ชื่อนิสิต นายพีรัช มาลินีกุล
ภาควิชา เคมี
ปีการศึกษา 2559

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

Titanosilicate porous thin film on silicon nanowire as catalyst for oxidation

ฟิล์มบางรูพรุนไทเทโนซิลิเกตบนเส้นลวดนาโนซิลิกอนเพื่อเป็นตัวเร่งปฏิกิริยาออกซิเดชัน

Mr. Peerat Malineekul

A Research submitted in Partial Fulfillment of the Requirements
For the Bachelor's Degree of Science in Chemistry
Department of Chemistry
Faculty of Science
Chulalongkorn University
Academic Year 2016

Project Title Titanosilicate porous thin film on silicon nanowire as catalyst for oxidation

Student Name Peerat Malineekul

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

COMMITTEE

M. Srisa-Art
.... Chairman

(Monpichar Srisa-art, Ph.D.)

Duangamol Tungasmita
... . Advisor

(Duangamol Tungasmita, Ph.D.)

.. .. Examiner

(Nattapong Paiboonvorachat, D.Phil.)

This Report has been Approved by Head of the Department of Chemistry

....Head of the Department of Chemistry

(Associate Professor Vudhichai Parasuk, Ph.D.)

Date................ May 2017

Quality of report ☑Very Good ☐Good ☐Fair

Project Title	Titanosilicate porous thin film on silicon nanowire as catalyst for oxidation	
Student Name	Peerat Malineekul	Student ID 5633120023
Advisor Name	Duangamol Tungasmita, Ph.D.	

Department of Chemistry, Faculty of Science, Chulalongkorn University, Academic Year 2016

Abstract

This research investigated the modification of silicon wafer substrate and preparation of titanium silicalite-1 thin film by using modified silicon nanowires as substrates. Silicon nanowires arrays were modified by using the metal-catalyzed electroless etching (MCEE) method. The length of silicon nanowires was linearly increased with etching time. Titanium silicalite-1 thin films were synthesized on modified silicon substrates using nanosized titanium silicalite-1 particles as seed by hydrothermal treatment. The film formation and catalytic properties were characterized using scanning electron microscope (SEM), X-ray diffractometer (XRD) and nitrogen adsorption-desorption isotherm. It was indicated that microporous materials with MFI structure showed good catalytic activity in the phenol hydroxylation with hydrogen peroxide. Titanium silicalite-1 thin film showed high phenol conversion and hydroquinone selectivity. Although iron-titanium silicalite-1 provided lower phenol conversion, it gave higher selectivity to catechol.

Keyword: thin film, titanium silicalite-1, silicon nanowires, zeolite

ชื่อโครงการ ฟิล์มบางรูพรุนไทเทโนซิลิเกตบนเส้นลวดนาโนซิลิกอนเพื่อเป็นตัวเร่งปฏิกิริยาออกซิเดชัน
ชื่อนิสิตในโครงการ นายพีรัช มาลินีกุล เลขประจำตัว 5633120023
ชื่ออาจารย์ที่ปรึกษา อาจารย์ ดร. ดวงกมล ตุงคะสมิต
ภาควิชาเคมี คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย ปีการศึกษา 2559

บทคัดย่อ

งานวิจัยชิ้นนี้ได้ทำการปรับปรุงแผ่นซิลิกอน และทำการสังเคราะห์ไทเทเนียมซิลิกาไลต์-1 ชนิดฟิล์มบาง โดยใช้เส้นลวดนาโนซิลิกอนสำหรับใช้เป็นชั้นฐานในการสังเคราะห์วัสดุฟิล์มบางนี้ เส้นลวดนาโนซิลิกอนเตรียมได้จากวิธีเมทอล-แคทาไลซ์ อิเล็กโทรเลส เอทชิ่ง โดยความยาวของเส้นลวดนาโนซิลิกอนมีแนวโน้มเพิ่มขึ้นอย่างคงที่ตามเวลาที่ใช้ในการทำปฏิกิริยา ไทเทเนียมซิลิกาไลต์-1 ชนิดฟิล์มบางสังเคราะห์ได้โดยใช้ไทเทเนียมซิลิกาไลต์-1 ที่มีขนาดอนุภาคระดับนาโนในการก่อผลึกร่วมกับการไฮโดรเทอร์มอล วัสดุที่สังเคราะห์ได้ถูกนำมาตรวจสอบลักษณะเฉพาะโดยใช้กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด เทคนิคการเลี้ยวเบนของรังสีเอ็กซ์ และการดูดซับแก๊สไนโตรเจน พบว่าวัสดุที่เตรียมได้มีรูพรุนระดับไมครอนและโครงสร้างแบบเอ็มเอฟไอ จากการนำวัสดุที่สังเคราะห์ได้นี้มาทดสอบความสามารถในการเร่งปฏิกิริยาออกซิเดชันของฟีนอลด้วยไฮโดรเจนเปอร์ออกไซด์พบว่าไทเทเนียมซิลิกาไลต์-1 ชนิดฟิล์มบางให้ค่าการเปลี่ยนแปลงของฟีนอลและการเลือกจำเพาะต่อไฮโดรควิโนนที่สูง เมื่อใช้เหล็กไทเทเนียมซิลิกาไลต์-1 ชนิดฟิล์มบาง พบว่าค่าการเปลี่ยนแปลงของฟีนอลลดน้อยลง แต่ให้ค่าการเลือกจำเพาะต่อแคทิคอลในปริมาณที่มากขึ้น

คำสำคัญ: ฟิล์มบาง, ไทเทเนียมซิลิกาไลต์-1, เส้นลวดนาโนซิลิกอน, ซีโอไลต์

Acknowledgement

In this opportunity, I would like to express my gratitude to my advisor, Dr. Duangamol Tungasmita for her helpful advices and on my research and her support.

I would like to gratitude to Dr. Monpichar Srisa-art and Dr. Nattapong Paiboonvorachat, senior project examination commitees, for sharing their useful advice and kindness.

I would like to thank Ms.Kusuma Sriyanai, Dr.Duangamol Jiraroj, researchers and all members in DT-WA lab for their help and solve my problems.

I also would like to gratitude to department of chemistry, faculty of science, Chulalongkorn university for the providing my opportunity and accommodation in laboratories.

Finally, I would like to thank my family and friends for a sincere support and plenty of good advices during my research.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

LIST OF ABBERVITATION

BET	Brunauer-Emmett-Teller
°C	Degree Celsius
g	Gram(s)
μm	Micrometer(s)
mL	Milliliter(s)
nm	Nanometer(s)
Ph	Phenol
BQ	Benzoquinone
HQ	Hydroquinone
CT	Catechol
XRD	X-ray diffraction
SEM	Scanning electron microscopy
TS-1	Titanium silicalite-1
Fe-TS-1	Iron-titanium silicalite-1

CHAPTER I

INTRODUCTION

1.1 Background

Catalysts are substances that help accelerate the process of chemical reactions. They provide an alternative pathway for breaking and forming new bonds without taking part in the reaction.[1] Catalysts are widely used in the chemical industry including petrochemical industries, petroleum refining, pharmaceutical industries and industrial research which enables the reduction of time and costs for manufacturing their products. The development of catalysts leads to fulfill the economical, political and environmental demands.[2]

Catalysts can be divided by phase into two main types; homogeneous and heterogeneous.[3] Homogeneous catalysts are presented in the same phase as the reactants and products. On the other hand, heterogeneous catalysts are presented in the different phase from the reactants and desired products are, loading to no complication in their separation.

Catalysts can also be classified by materials such as zeolites, metal and chemical compounds. Considered with environmentally friendly, economical and production processes, a heterogeneous catalyst, such as zeolite played a significant role for the selective oxidation reactions and advantage mild conditions in refineries and chemical industries, such as oxidation of alcohol,[4] olefin and aromatic.[5] Phenol hydroxylation with oxidizing agent gave many important products such as bisphenol A, adipic acid, phenol resin, alkyl phenol and caprolactam.[6] Also, hydroquinone and catechol which were prepared by direct hydroxylation of phenol with hydrogen peroxide as an oxidizing agent are widely used as perfumes, pharmaceuticals, antioxidants and so on.

Normally, zeolites can be prepared as crystalline powder but they got a problem with the pressure when operated in a continuous flow reactor. Nowadays, zeolite thin film become more popular in many industrial applications, such as sensors,[7-8] membranes,[9] electronic devices[10] and catalyst.[11] The catalyst thin film can be synthesized by seeding the zeolite nanocrystals on the substrate and hydrothermal synthesis.

1.2 **Theory**

1.2.1 Zeolites[12]

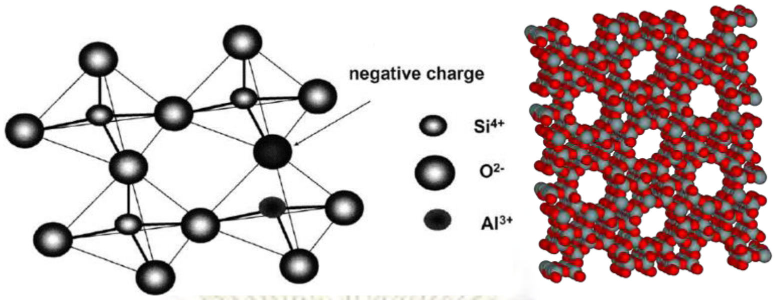


Figure 1.1 Structure of zeolites.[13]

Zeolites are microporous crystalline aluminosilicates. A unit cell consists of one silicon (or aluminium) and 4 oxygen atoms in their framework, which is related to a three-dimensional network of SiO_4 or AlO_4 tetrahedral and share oxygen ions for linked formation with empirical formulas of $[SiO_2]$ and $[AlO_2]^-$. The negative charge could be balanced by metal groups IA (alkaline) and IIA (alkaline earth). A general unit cell formula of zeolite is

$$M_{x/n}[(AlO_2)_x(SiO_2)_y.zH_2O]$$

where M is an extra-framework metal of valence n, x and y represent the total amounts of tetrahedra in a unit cell and z is the number of water molecules. The exact amount of x+y is specific for each zeolite structure, for examples, 96 for MFI and 192 for FAU structures. The three-dimensional tetrahedral frameworks are referred as the primary building units (PBUs) and they are assembled to become secondary building units (SBUs) as shown in Figures 1.2 and 1.3. The number of tetrahedral frameworks are related to the number of oxygen atoms thought the dark spots in Figure 1.3 which indicates the pore size of zeolite. Small-pore zeolites such as zeolite A consist of 8 rings with pore size of 0.30 to 0.45 nm in diameter. ZSM-5 and TS-1 zeolites are examples of medium-pore zeolites consisting of 10 rings with pore size of 0.45 to 0.60 nm in diameter and large-pore zeolites have 12 rings with pore size of 0.6 to 0.8 nm in diameter.

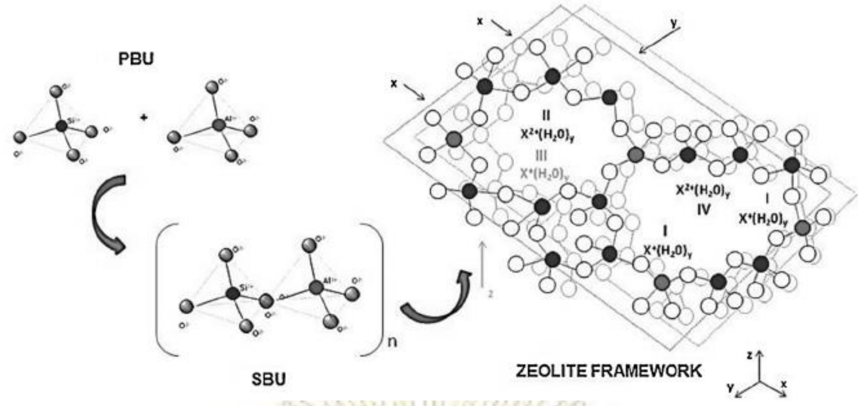


Figure 1.2 (a) primary building unit (PBU), (b) secondary building unit (SBU) and (c) zeolite framework.[14]

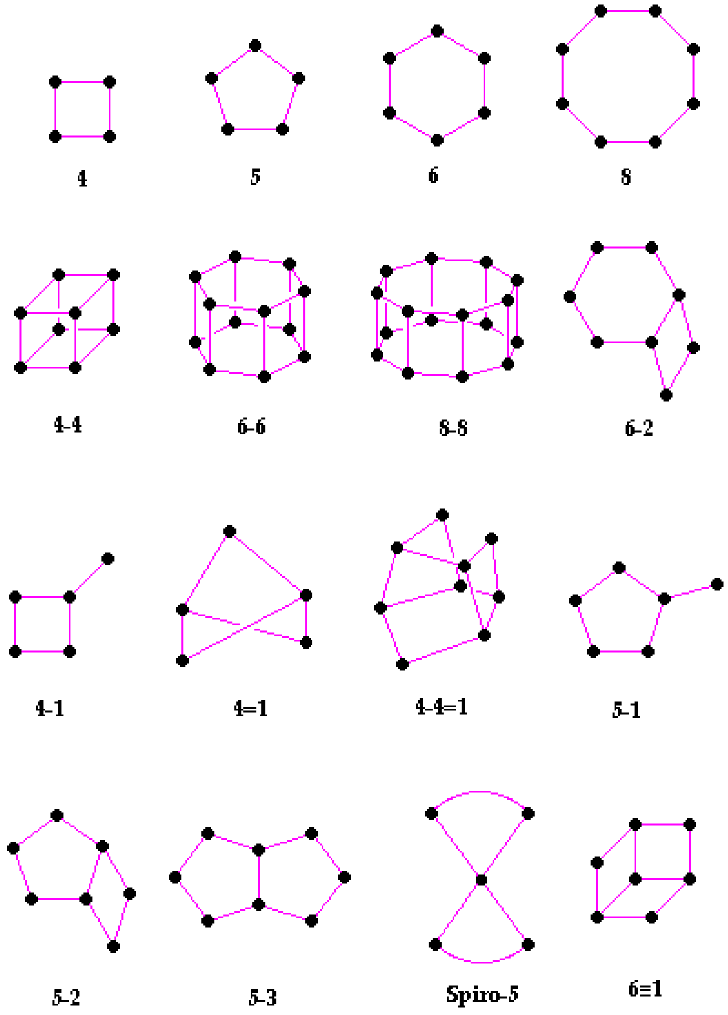


Figure 1.3 Secondary building units (SBUs) of zeolites.[15]

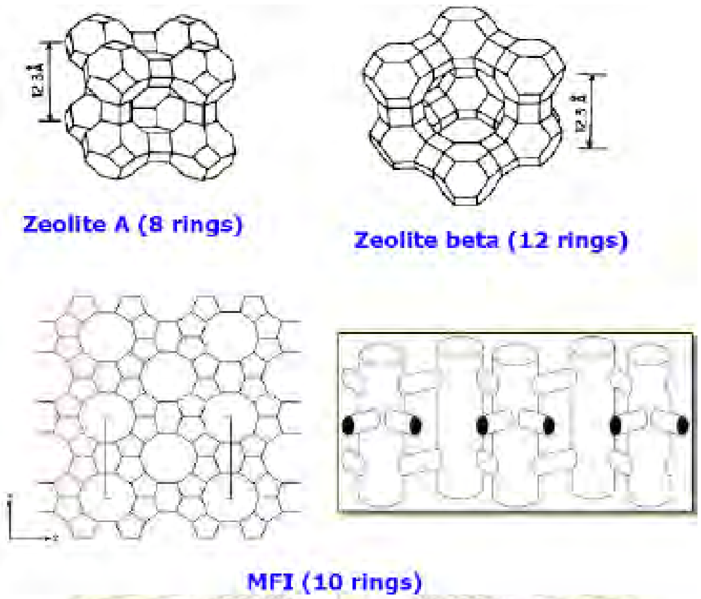


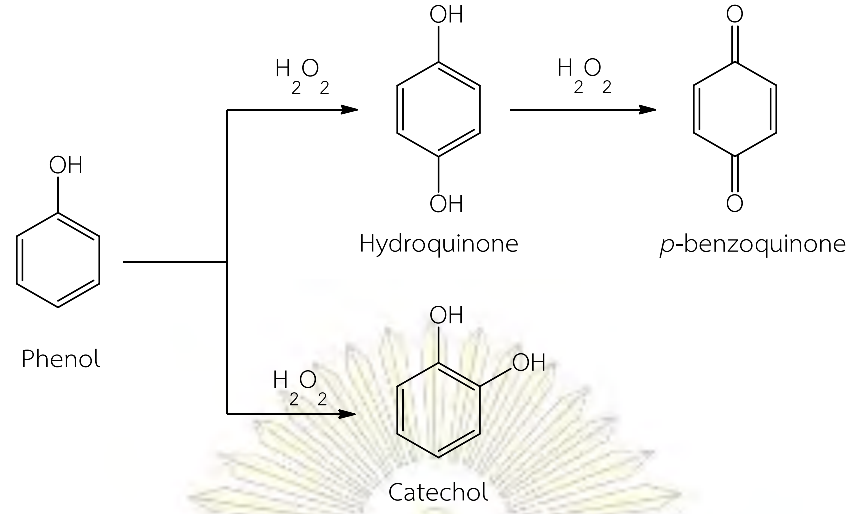
Figure 1.4 Three types of pore opening in zeolite framework.[16]

1.2.2 Titanium silicalite-1[17]

Titanium silicalite-1 (TS-1) was discovered by Taramasso in 1983. Its catalytic properties involving the use of hydrogen peroxide as oxidizing agent in oxidation reaction has been widely used. It has MFI framework which contains two types of intersection channels: straight and zigzag channels. Straight channel has elliptical opening and run parallel to b-axis of the orthorhombic unit cell. Zigzag has near circular opening, is sinusoidal and schematic of three-dimension channel.

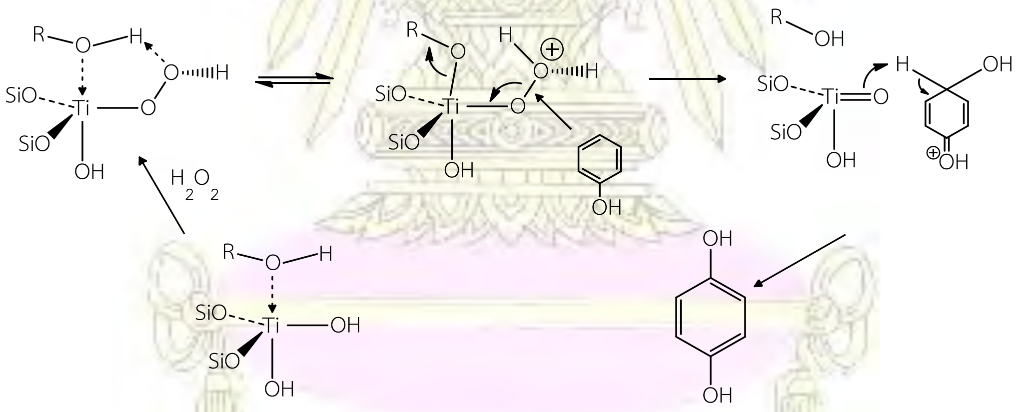
1.2.3 Phenol oxidation[18]

Phenol oxidation (also known as phenol hydroxylation) is an important reaction for industrial chemistry. Phenol reacts with hydrogen peroxide to give hydroquinone and catechol as the main products which are widely used as perfumes, pharmaceuticals, medicines, antioxidants and for organic synthesis.

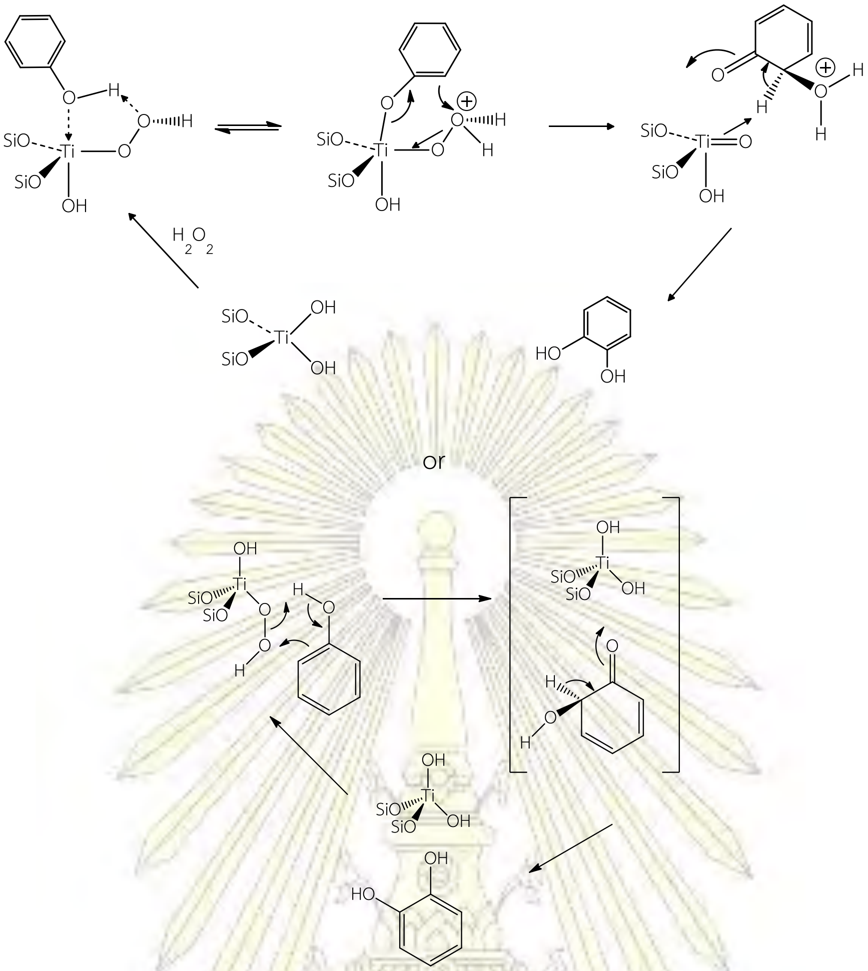


Scheme 1.1 Phenol hydroxylation with hydrogen peroxide.[19]

Phenol oxidation can be generated with ecologically and friendly process by using catalysts. A homogeneous catalyst, such as mineral acid, simple metal ions and their complexes was a disadvantage for separating catalyst from the product. So, heterogeneous catalysts such as metal oxide, supported metal oxide, and mesoporous material which hold a better performance in separating catalysts from products and reactants have been widely studied in recent years.[20]



Scheme 1.2 Proposed reaction mechanism for the formation of hydroquinone in phenol hydroxylation.[21]



Scheme 1.3 Proposed reaction mechanism for the formation of catechol in phenol hydroxylation.[22]

1.2.4 Silicon nanowires[23]

Silicon nanowires were prepared from silicon precursor by etching of a solid. Metal-catalyzed electroless etching (MCEE) method has been used in the fabrication of vertical silicon nanowires arrays. Figure 1.5 shows the process of the MCEE method. First, silicon is continuously galvanic displaced by Ag ion through the first reaction (1) which is an anodic reaction. The Ag ion attracts the electrons from the valence band of Si and turns itself into the solid Ag particle on the Si surface, the second reaction (2, cathodic reaction) takes place in which an oxidized silicon forms the SiO_2 around the Ag/Si interface shown in black color in Figure 1.5b.For the last step, SiO_2 is etched away by HF in the etching solution, resulting in a shallow pit underneath the Ag particle and the captured Ag particle sinks downward to the bottom of the pit.

$$Ag^+ + e^- \longrightarrow Ag^0(s) \qquad (1)$$

$$Si(s) + 2H_2O \longrightarrow 2SiO_2(s) + 4H^+ + 4e^- \qquad (2)$$

$$SiO_2(s) + 6HF \longrightarrow H_2SiF_6 + 2H_2O \qquad (3)$$

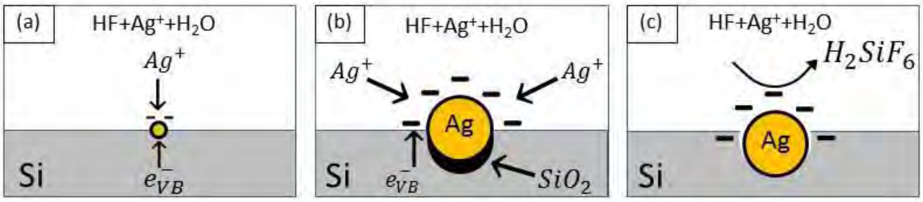


Figure. 1.5 Diagram of the MCEE method.

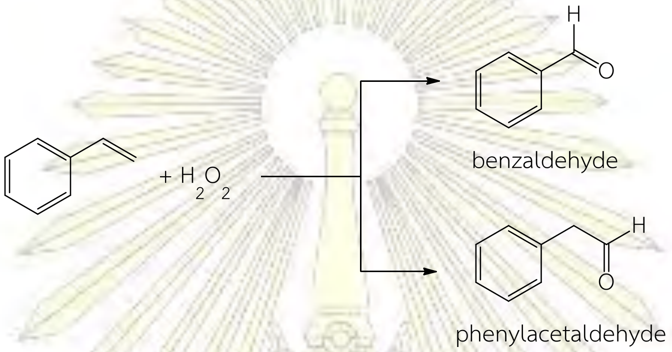
1.3 Literature reviews

In 1983, titanium silicalite-1 was discovered by Taramasso.[24] In general, titanium silicalite-1 was synthesized from silicon and titanium compounds such as tetraethylorthosilicate (TEOS), silicon dioxide (SiO_2), tetraethylorthotitanate (TEOT) or tetrabutylorthotitanate (TBOT) as silica and titanium sources, respectively and using an organic base such as tetrapropylammonium hydroxide (TPAOH) or tetrapropylammonium bromine (TPABr) as a structure directing agent (organic template). The gel composition of titanium silicalite-1 is composed of the various amount of silicon and alumina sources, organic base and water. All chemical compounds were mixed together and became homogeneous, ready for crystallization. Crystallization by hydrothermal process requires the exact temperature between 130°C and 200°C. The longer crystallization time and the higher temperature, the larger crystal size was formed. Finally, the crystals were calcined at 550°C. Titanium silicalite-1 can also be synthesized by seeding to give the smaller crystals, which can increase catalytic activity.

Zhang et al.[25] reported the preparation of titanium silicalite-1 at a low molar ratio of $TPAOH/SiO_2$, which could be reduced to 0.05 and showed as an excellent catalytic performance in the epoxidation of 1-hexene by hydrogen peroxide. The low usage of TPAOH and using inorganic silica as a silica source could reduce the costs of titanium silicalite-1.

Zuo et al.[26] synthesized small crystals of titanium silicalite-1 by using the mother liquid of TS-1 nano-size as seed and using TPABr-ethylamine as structure directing agent. The crystal size depends on the amount of seed. The more amount of seed was used, the larger crystal was obtained. This catalyst gave high performance in the epoxidation of propylene and high conversion of phenol in hydroxylation of phenol.

Qiu et al.[27] prepared titanium silicalite-1 film on porous ceramic tubes using silicalite-1 as seed and followed by hydrothermal synthesis. The surface tube was completely coated with TS-1 seed and provides nucleation sites for zeolite crystallization. TS-1 film was uniformly grown on the seed layer. This TS-1 catalyzed the oxidation of styrene to phenylacetaldehyde and benzaldehyde with hydrogen peroxide as an oxidizing agent.



Scheme 1.4 Styrene hydroxylation with hydrogen peroxide.

Wang et al.[28] prepared titanium silicalite-1 catalytic films on porous Al_2O_3 tubes, using silicalite-1 nanoparticle as a seed by hydrothermal treatment. These catalytic films were used in phenol hydroxylation with hydrogen peroxide. It was indicated that the crystallization time of titanium silicalite-1 films has an effect on films thickness and its morphology. However, the ratio of Ti/Si also influenced the content of titanium atom incorporated as a framework and was correlated with the activity. Most reaction occurred in a shallow layer near the film due to the mass transfer effects in the titanium silicalite-1 films.

Mei et al.[29] modified titanium silicalite-1 by doping 1% of various metals (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and La) as catalysts into titanium silicalite-1 to catalyzed the reaction of butadiene epoxidation with hydrogen peroxide. They found that V, Cr and Mn caused hydrogen peroxide decomposition even the conversion was high, but its utilization was relatively low. The introduction of Fe, Co, Ni and La into TS-1 promoted a good activity in butadiene epoxidation. These metals changed the electronic environment of Titanium active site in TS-1 to some extent via a five-membered ring intermediate.

Objectives

1. Synthesize and characterize titanium silicalite-1 and iron-titanium silicalite-1 thin film.
2. Examine the synthesized catalysts using the reaction of phenol hydroxylation with hydrogen peroxide in a microflow reactor.

CHAPTER II

EXPERIMENTAL

2.1 Instruments, apparatus and analytical techniques

2.1.1 Scanning electron microscope (SEM)

Scanning electron microscope (JSM-5410 LV) was used to analyze the morphology, elementals composition and determine the particle size. The thin films samples were coated with sputtering gold under vacuum for conductivity.

2.1.2 X-ray diffraction (XRD)

X-ray diffraction was used to characterize the patterns of materials. A Rigaku D/MAX-2200 Ultima$^+$ diffractometer equipped with monochromater at 2-theta angle between 5 to 50 degrees and Cu K$_\alpha$ radiation source (40 kV, 30 mA)

2.1.3 Microflow reactor

The reactant mixture was flowed to a column reactor with thin films catalysts. The oxidation of phenol occurs in a column. The column’s diameter and height are 0.6 cm and 10 cm, respectively.

2.1.4 Gas Chromatography

The amount of final products were analyzed by gas chromatography, using cycloheptanone as an internal standard.

2.1.5 Nitrogen adsorption-desorption

Nitrogen adsorption-desorption isotherm, specific surface area and pore size distribution of the material were analyzed by BEL Japan, BELSORP-moni instrument. The samples weighted precisely after being pretreated at 400°C for 3 hours.

2.2 Chemicals

1. Trichloroethylene (Unilab, 95%)

2. Acetone (RCI Labscan)

3. Methanol (Merck, 99.9%)

4. Hydrofluoric acid (Merck, 48%)

5. Ethanol (Merck, 99.9%)

6. Sulfuric acid (Merck, 95-98%)

7. Hydrogen peroxide (Merck, 30%)

8. Nitric acid (Merck, 65%)

9. Silver nitrate (Merck)

10. 3-Mercaptopropyl trimethoxysilane (MPTMS), (Aldrich, 95%)

11. Tetrapropyl ammonium hydroxide (TPAOH), (Merck, 40%)

12. Tetraethyl orthosilicate (TEOS), (Merck, 99%)

13. Tetraethyl orthotitanate (TEOT), (Merck, 95%)

14. Isopropanol (Univar)

15. Tetrabutyl orthotitanate (TBOT), (Aldrich, 97%)

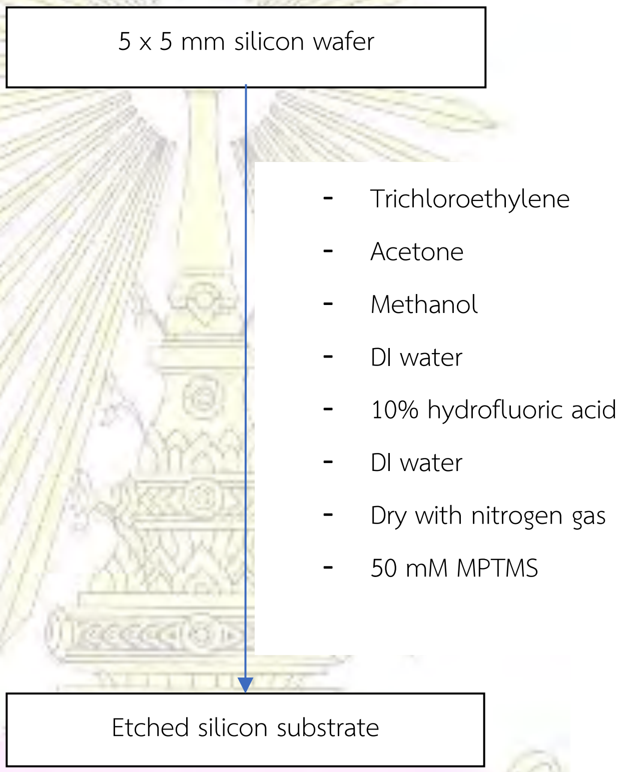
16. Iron (III) nitrate nonahydrate (Merck)

16. Phenol (Aldrich)

17. Cycloheptanone (Aldrich, 99%)

2.3 Preparation of silicon wafer substrates

Silicon wafer substrates were cut with a diamond pen into a piece of 5 x 5 mm. The substrates were clean and ultrasonicated with trichloroethylene, acetone, methanol and DI water for 10 minutes in each step, respectively. Then, the surface of substrates was etched in 10% of hydrofluoric acid for 15 seconds. After that, the substrates were rinsed with DI water and dried with nitrogen gas. Finally, the substrates were treated with 50 mM of 3-mercaptopropyl trimethoxysilane for 10 minutes and dried the substrates at 170°C for 2 hours.

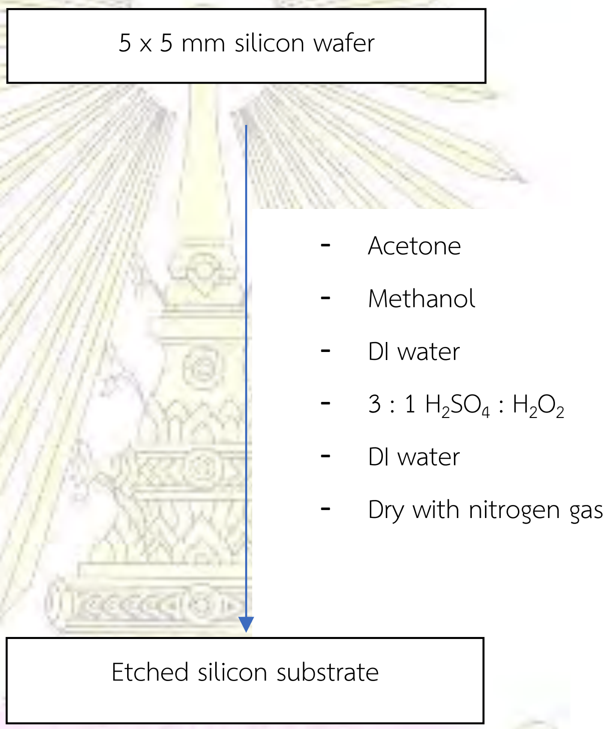


Scheme 2.1 Preparation of silicon substrates.

2.4 Preparation of silicon nanowires substrates

2.4.1 Pre-cleaning step

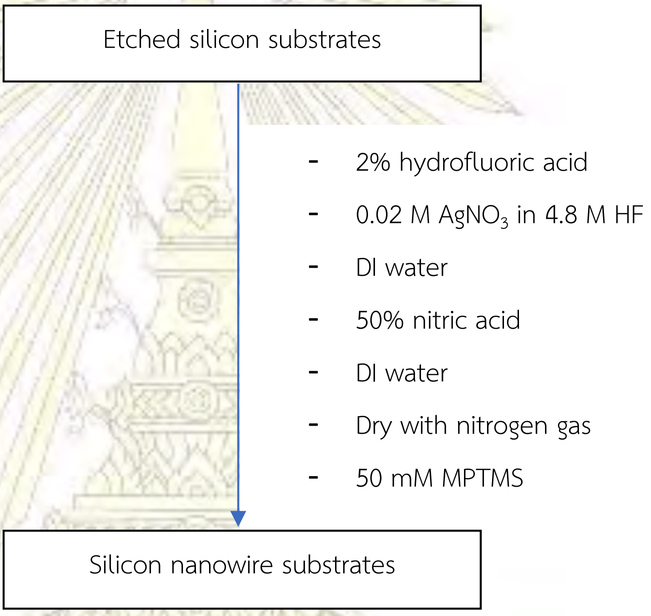
Firstly, silicon substrates were washed with acetone for 10 minutes to remove organic on the surface. The substrates were washed off by ethanol for 10 minutes and rinsed with DI water for 10 minutes three times. Metal particles on the silicon substrates were removed by immersing in the mixture solution of sulfuric acid and hydrogen peroxide in the ratio of 3:1. Then, the substrates were washed with DI water and dried with nitrogen gas.



Scheme 2.2 Pre-cleaning method before etching step.

2.4.2 Etching step

Firstly, oxide layers on the surface were removed by dipping the substrates into 2% of hydrofluoric acid in Teflon cup for 2 minutes. Then, the silicon substrates etched in the mixture solution of 50 mL 0.02 M silver nitrate and 50 mL 4.6 M hydrofluoric acid. The silicon nanowires will be presented. After that, the silicon nanowire substrates were rinsed twice with DI water to stop the etching reaction and silver layers were removed with 50% nitric acid for 5 minutes. The silicon nanowire substrates were cleaned with DI water. Finally, the nanowire substrates were treated with 50mM of 3-mercaptopropyl trimethoxysilane for 10 minutes and dried at 170°C for 2 hours.

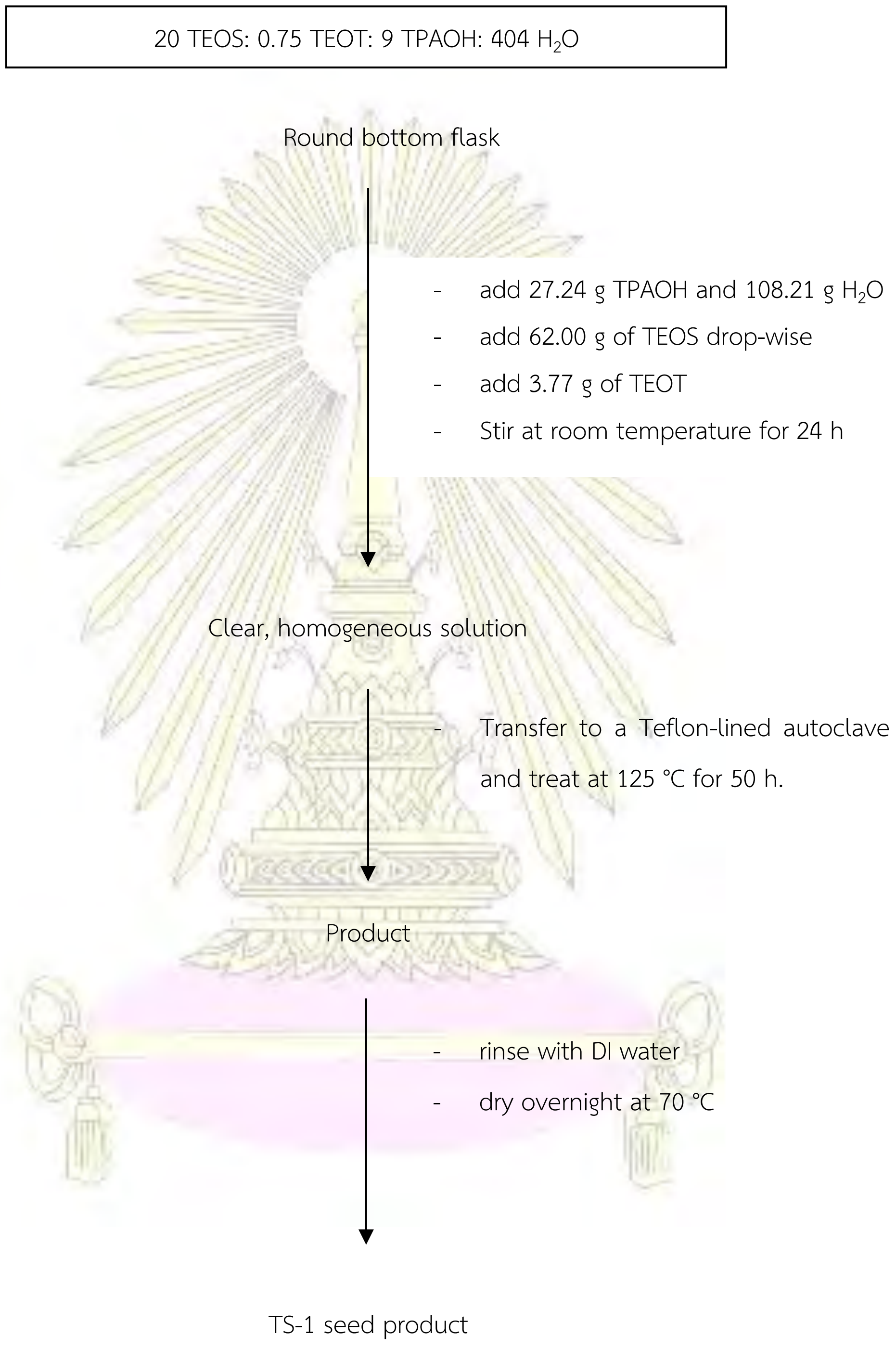


Scheme 2.3 Etching step to form silicon nanowires.

2.5 Synthesis of titanium silicalite-1 films

2.5.1 Preparation of titanium silicalite-1 seed

The preparation of titanium silicalite-1 seed was carried out according to the procedure reported in the literature.[30] Then, 27.24 g tetrapropylammonium hydroxide (TPAOH) was dissolved in 108.21 g DI water under stirring. 62.00 g tetraethylorthosilicate (TEOS) and 3.77 g tetraethylorthotitanate (TEOT) were added to the solution. A homogeneous solution with a molar composition of 20 TEOS: 0.75 TEOT: 9 TPAOH: 404 H_2O was obtained after vigorous stirring at room temperature for 24 hours. After that, A homogeneous solution was transferred into a Teflon-lined autoclave for hydrothermal treatment at 125°C for 50 hours. Rinse the white solid product with DI water and dry the product at 70°C overnight.



20 TEOS: 0.75 TEOT: 9 TPAOH: 404 H_2O

Round bottom flask

- add 27.24 g TPAOH and 108.21 g H_2O
- add 62.00 g of TEOS drop-wise
- add 3.77 g of TEOT
- Stir at room temperature for 24 h

Clear, homogeneous solution

- Transfer to a Teflon-lined autoclave and treat at 125 °C for 50 h.

Product

- rinse with DI water
- dry overnight at 70 °C

TS-1 seed product

Scheme 2.4 Preparation of titanium silicalite-1 seed.

2.5.2 Seed deposition onto the substrates

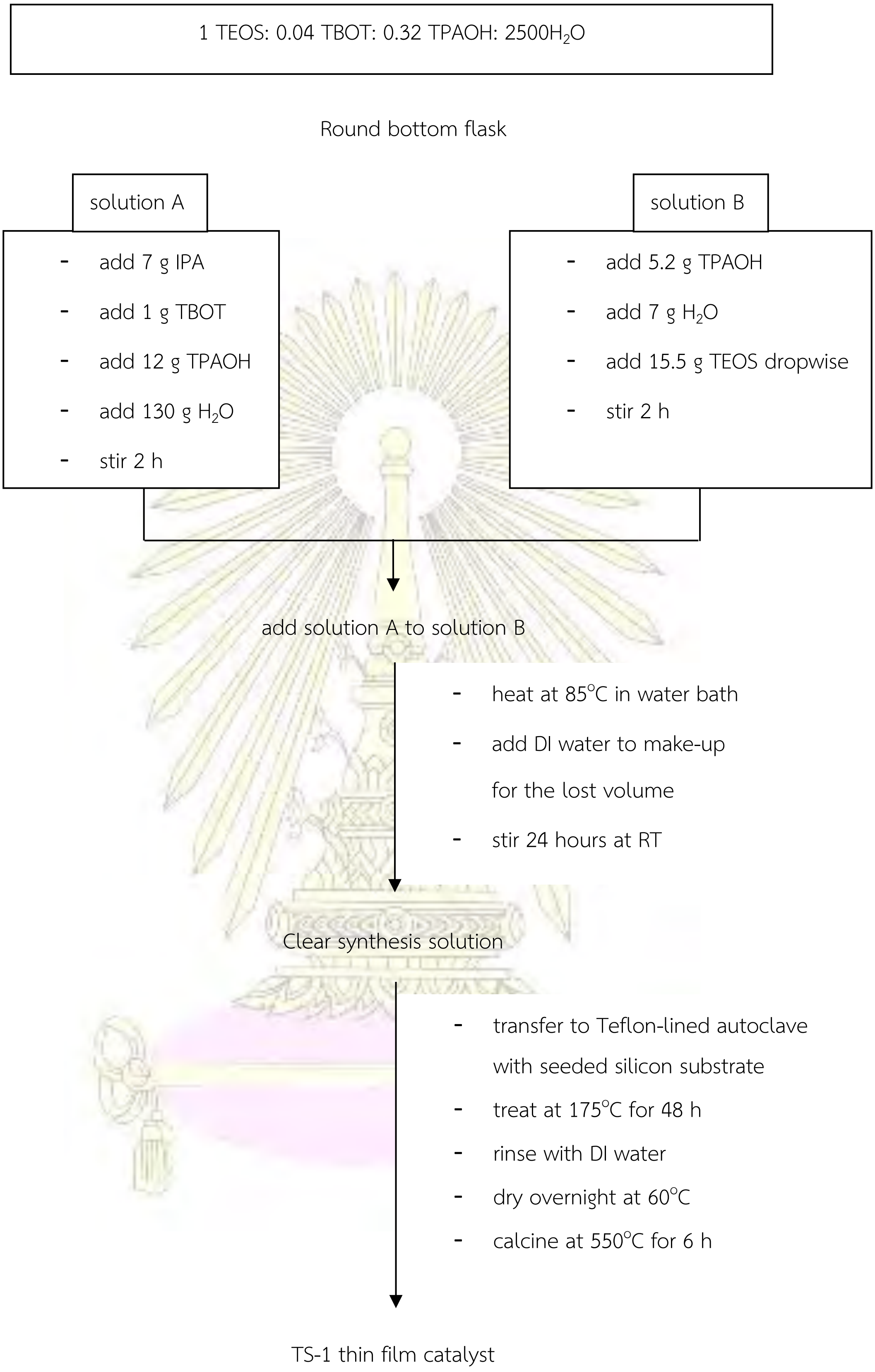
Silicon substrates or silicon nanowires substrates were immersed in absolute ethanol which contained 2%wt of TS-1 seed for an hour and dry the substrates at 60°C overnight. Finally, the substrates with TS-1 seed were calcined at 550°C for 6 hours.

2.5.3 Preparation of titanium silicalite-1 films (TS-1 film)

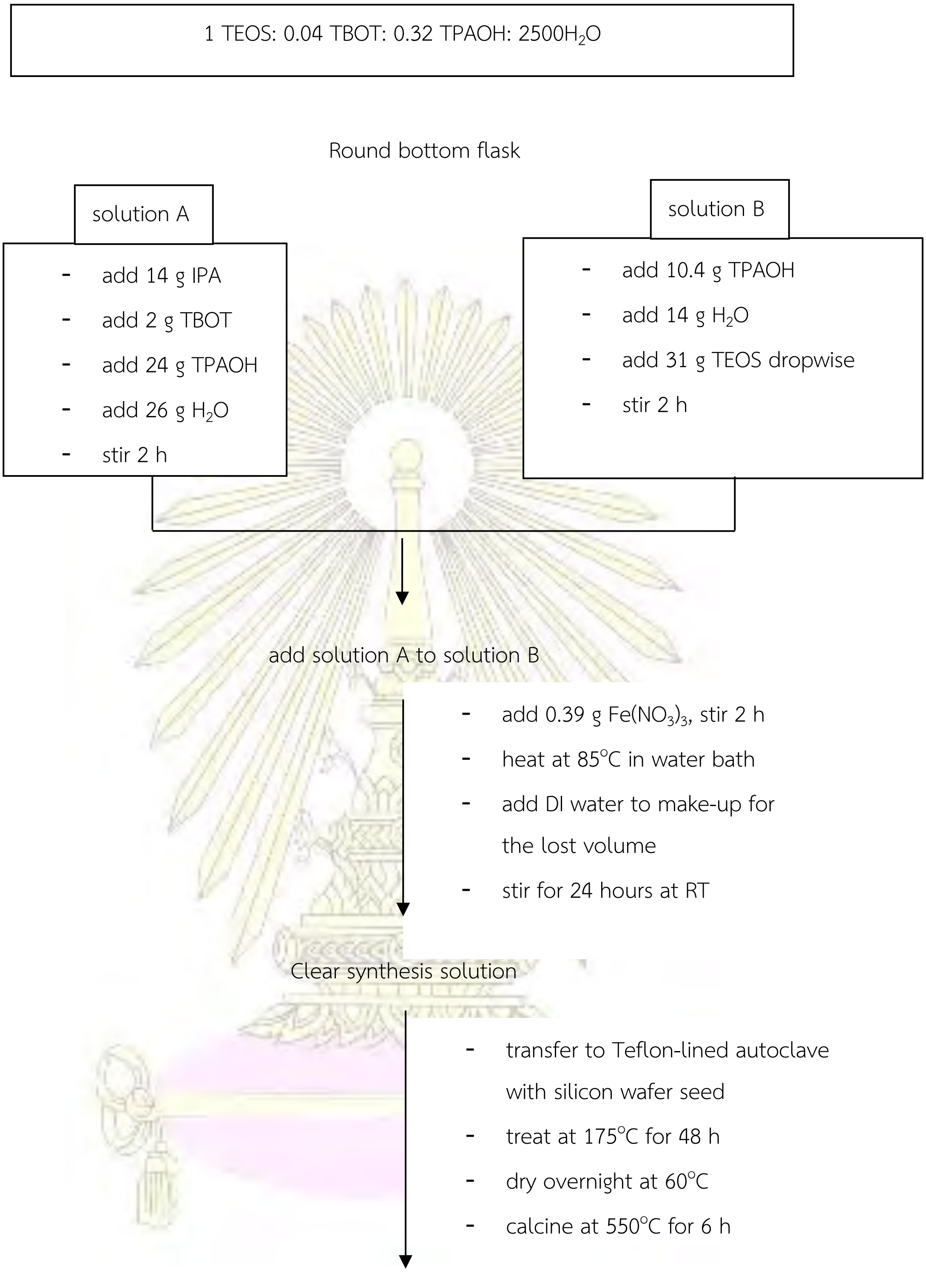
The titanium silicalite-1 films were prepared according to the procedure reported in the previous work.[28] Firstly, prepare solution A which contained 7 g isopropanol, 1 g tetrabutyl orthotitanate (TBOT), tetrapropylammonium hydroxide (TPAOH) and 130 g DI water under stirring for 2 hours. Then prepare solution B by adding 15.5 g tetraethylorthosilicate (TEOS) dropwise to the mixture of 5.2 g tetrapropylammonium hydroxide and 70 g DI water under stirring for 2 hours. After solution A and B were homogeneous, transfer solution A into solution B and heat in water bath at 85°C to evaporate alcohol and add DI water to make-up for the lost volume. A homogeneous solution with the molar composition of 1 TEOS: 0.04 TBOT: 0.32 TPAOH: 2500 H_2O was obtained after vigorous stirring at room temperature for 24 hours. Transfer the homogeneous solution with the silicon/silicon nanowires substrates to the Teflon-lined autoclave and treat at 175°C for 48 hours. Finally, rinse titanium silicalite-1 films with DI water, dry at 60°C overnight and calcine at 550°C for 6 hours.

2.5.4 Preparation of iron titanium silicalite-1 film (Fe-TS-1 film)

The preparation of Fe-TS-1 film was almost similar to the preparation of TS-1 film. The addition step is to add 0.39 g of $Fe(NO_3)_3.9H_2O$ after solution A and B were mixed together and keep stirring at room temperature for 2 hour. A homogeneous solution obtained molar composition of 1 TEOS: 0.04 TBOT: 0.01 $Fe(NO_3)_3$: 0.32 TPAOH: 2500 H_2O.



Scheme 2.5 Preparation of titanium silicalite-1 thin film



1 TEOS: 0.04 TBOT: 0.32 TPAOH: 2500H_2O

Round bottom flask

solution A

- add 14 g IPA
- add 2 g TBOT
- add 24 g TPAOH
- add 26 g H_2O
- stir 2 h

solution B

- add 10.4 g TPAOH
- add 14 g H_2O
- add 31 g TEOS dropwise
- stir 2 h

add solution A to solution B

- add 0.39 g $Fe(NO_3)_3$, stir 2 h
- heat at 85°C in water bath
- add DI water to make-up for the lost volume
- stir for 24 hours at RT

Clear synthesis solution

- transfer to Teflon-lined autoclave with silicon wafer seed
- treat at 175°C for 48 h
- dry overnight at 60°C
- calcine at 550°C for 6 h

Fe-TS-1 thin film catalyst

Scheme 2.6 Preparation of iron titanium silicalite-1 thin film

2.6 Catalytic activity test for the oxidation of phenol

For the oxidation of phenol in continuous flow reactor, catalysts thin films were contained into the column reactor. The reactant mixture was prepared by adding 0.94 g phenol, 2.28 g hydrogen peroxide and 10.8 g DI water into the Erlenmeyer flask. The ratio of phenol: H_2O_2 is 1: 2. Reactant mixture was kept in cooler and covered the flask with opaque container. The reactant mixture was introduced into the reactor of 4 μL/min at $60^{\circ}C$. All products were analyzed by gas chromatography.

CHAPTER III

RESULTS AND DISCUSSION

3.1 Characterization of materials

3.1.1 Scanning electron microscopy

3.1.1.1 Effect of etching time on the formation of silicon nanowires

Silicon substrates were etched in silver solution to form silicon nanowires arrays for preparing the thin film catalyst. Figure 3.1 shows representative cross-sectional scanning electron micrographs of the silicon nanowires with different etching time: 3, 5, 10, 15 and 30 minutes. The results show the average lengths of each substrate: 57 µm, 64 µm, 83 µm, 122 µm and 270 µm, respectively. The etching rate is approximately 8 µm/min. The average length of silicon nanowires linearly increases with the etching time.

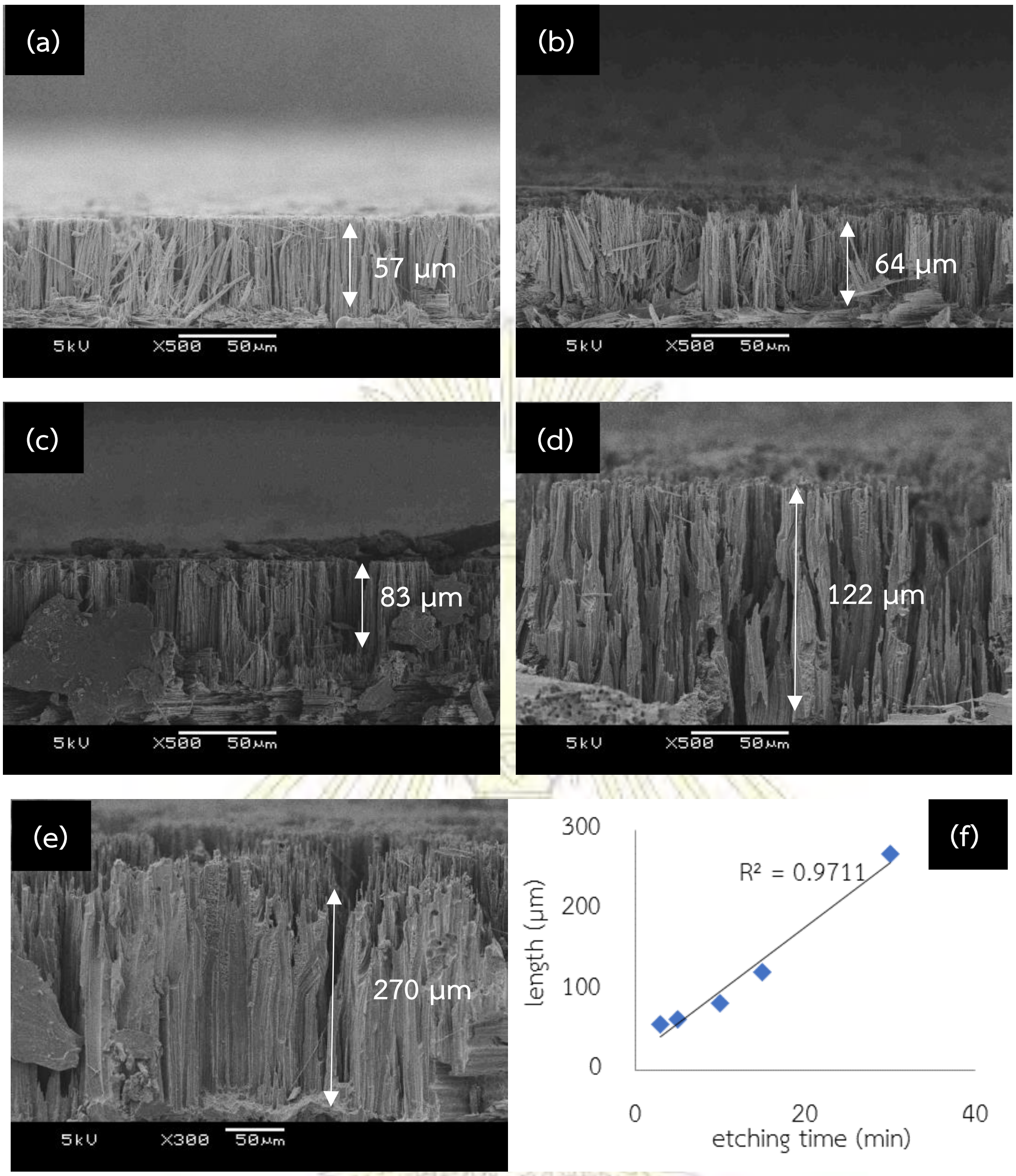


Figure 3.1 Cross-sectional scanning electron micrographs of the silicon nanowires with different etching time (a) 3, (b) 5, (c) 10, (d) 15, (e) 30 minutes and (f) the relationship between the lengths of the silicon nanowires and etching time.

In Figure 3.2 top-view scanning electron micrographs of the silicon nanowires with different etching time conditions: 3, 5, 10, 15 and 30 minutes, respectively. The longer etching time of nanowires are slightly bended towards to the others and form the bundle structure instead of vertically aligned individual nanowires. This could be attributed to the flexibility of the nanowires, Van der Walls forces become dominant and hold nanowires together.[31]

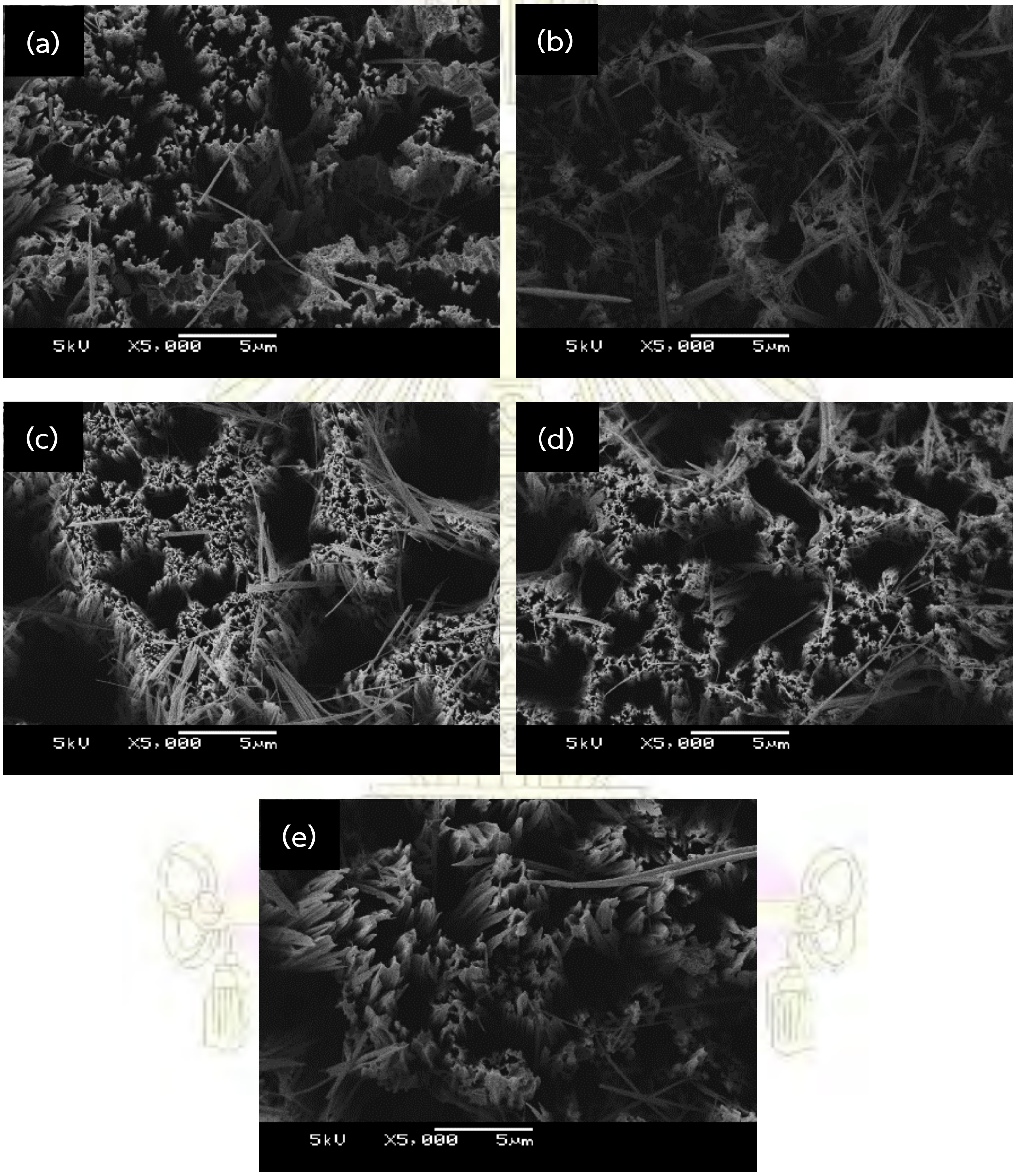


Figure 3.2 Top view scanning electron micrographs of the silicon nanowires with different etching time (a) 3, (b) 5, (c) 10, (d) 15 and (d) 30 minutes.

3.1.1.2 Titanium silicalite-1 thin films on silicon substrates

Titanium silicalite-1 was deposited on silicon substrates as shown in Figure 3.3a. The thickness of the thin film is approximately 300 μm. Titanium silicalite-1 dense thin film demonstrated hexagonal structure with 1 μm length and 0.4 μm width.

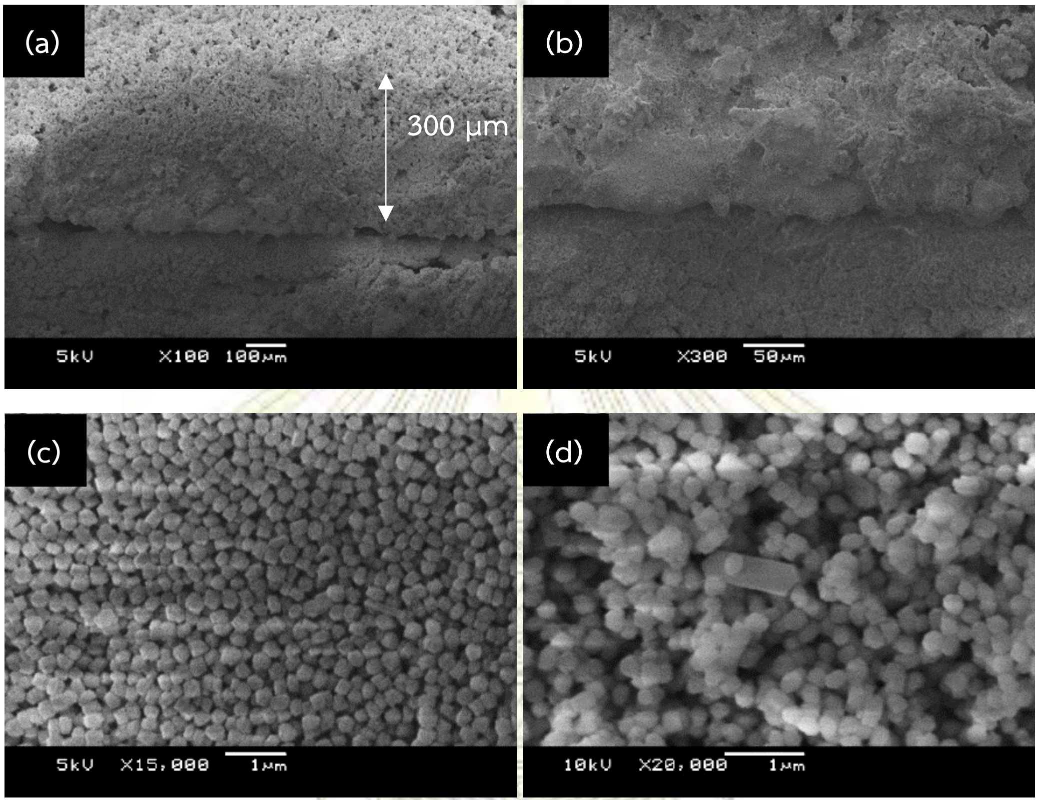


Figure 3.3 Scanning electron micrographs of TS-1 thin film on silicon substrates (a)-(b) cross-sectional; (c)-(d) top-view.

3.1.1.3 Titanium silicalite-1 thin films on silicon nanowires substrates

In this work, silicon nanowires which were etched for 30 minutes have been considered to be used as substrates due to the highest surface area, the more amount of crystals seeds can be deposited on the substrates can promote the formation of small and uniform crystals. After depositing of titanium-silicalite-1 seeds on silicon nanowires substrates, the seeds show a good cohesion with silicon nanowires. Seeds can fulfil the space of the silicon nanowires arrays. The sphere particles are approximately 0.2 µm average in diameter.

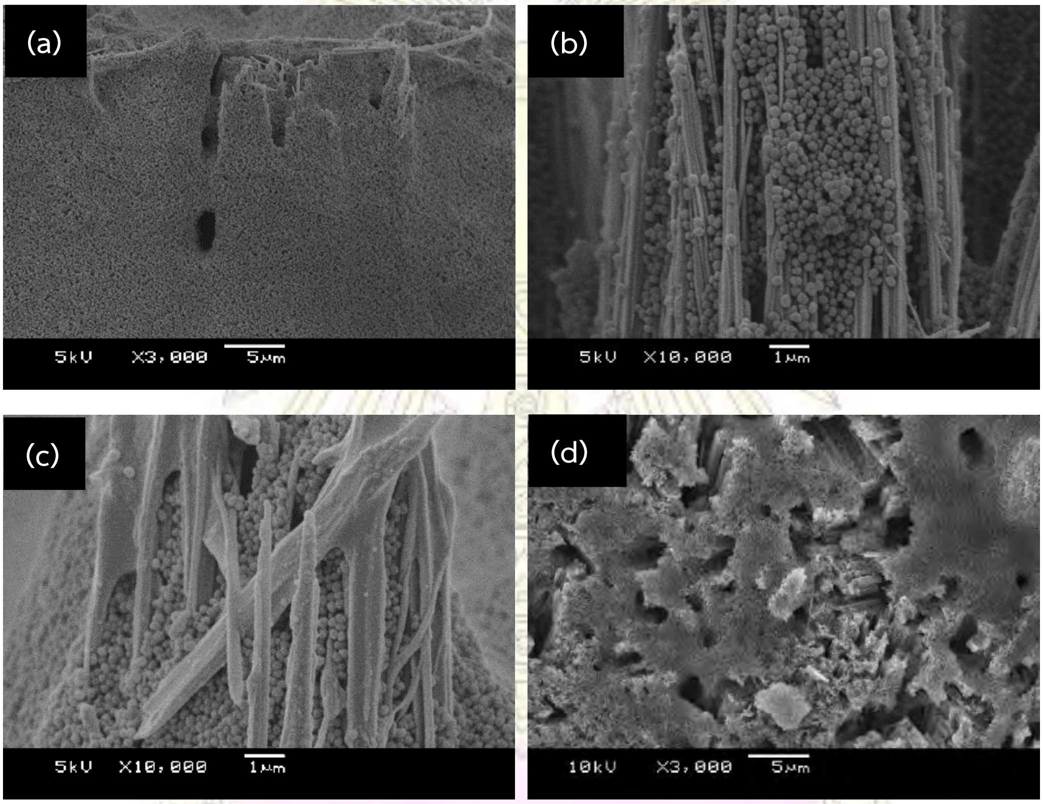


Figure 3.4 Scanning electron micrographs of TS-1 seeds deposited on silicon nanowire substrates (a)-(c) cross-section; (d) top-view.

After hydrothermal treatment, titanium silicalite-1 thin films were formed. Figure 3.5 show the morphology of staurolite-liked crystals with the average dimension of 1 μm length and 0.2 μm width and the film thickness is 200 μm.

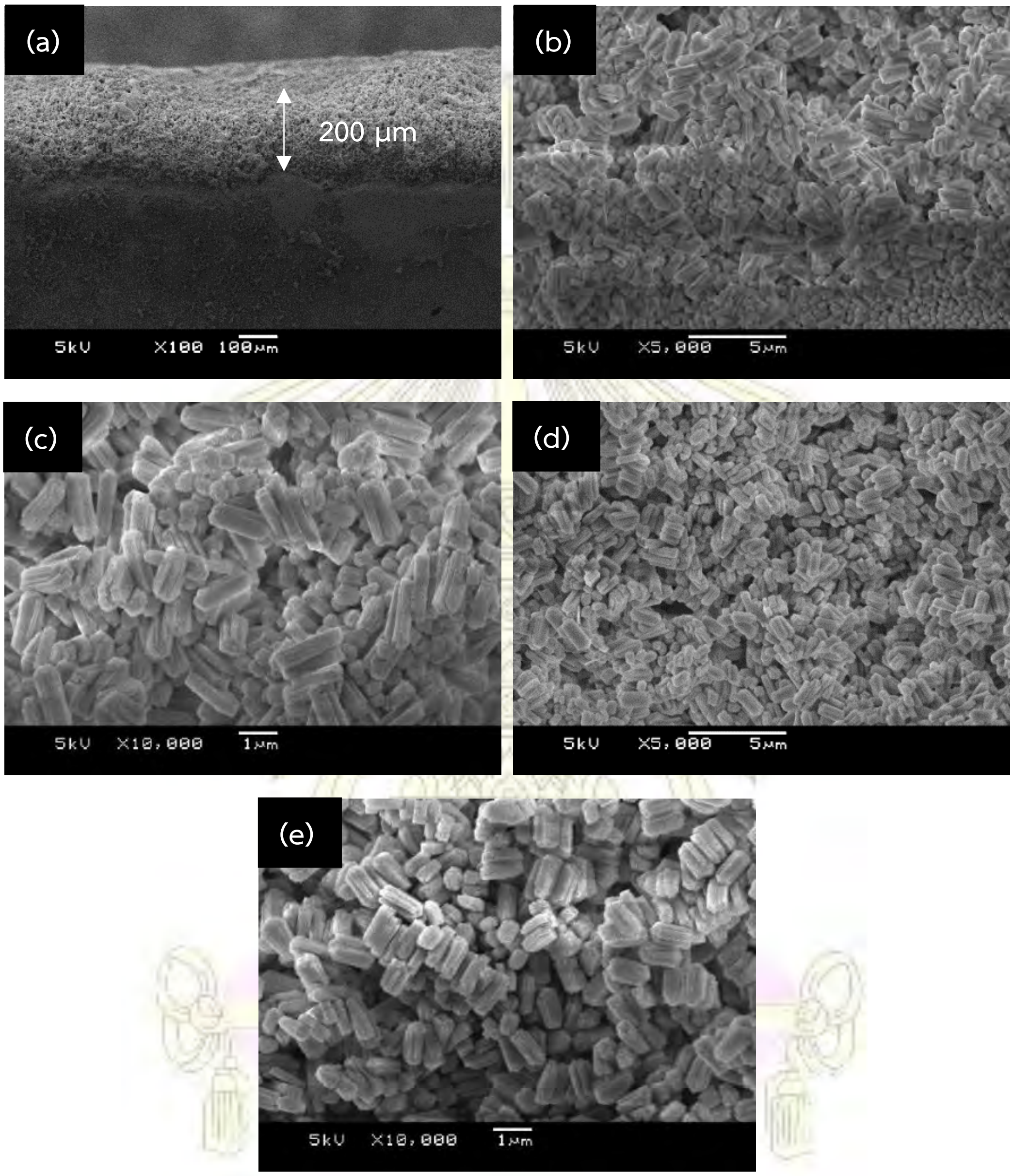


Figure 3.5 Scanning electron micrographs of TS-1 thin film on silicon nanowire substrates (a)-(c) cross-section; (d)-(e) top view.

3.1.1.4 Iron-titanium silicalite-1 thin films on silicon nanowires substrates

Figure 3.6 shows micrographs of iron-titanium silicalite-1. The catalysts grew smoothly on the silicon films with the thickness of 200 μm. the crystal represented blade-liked shape. The average dimension is 4 μm long and 0.8 μm wide. The crystals are larger than titanium silicalite-1 due to their identities.

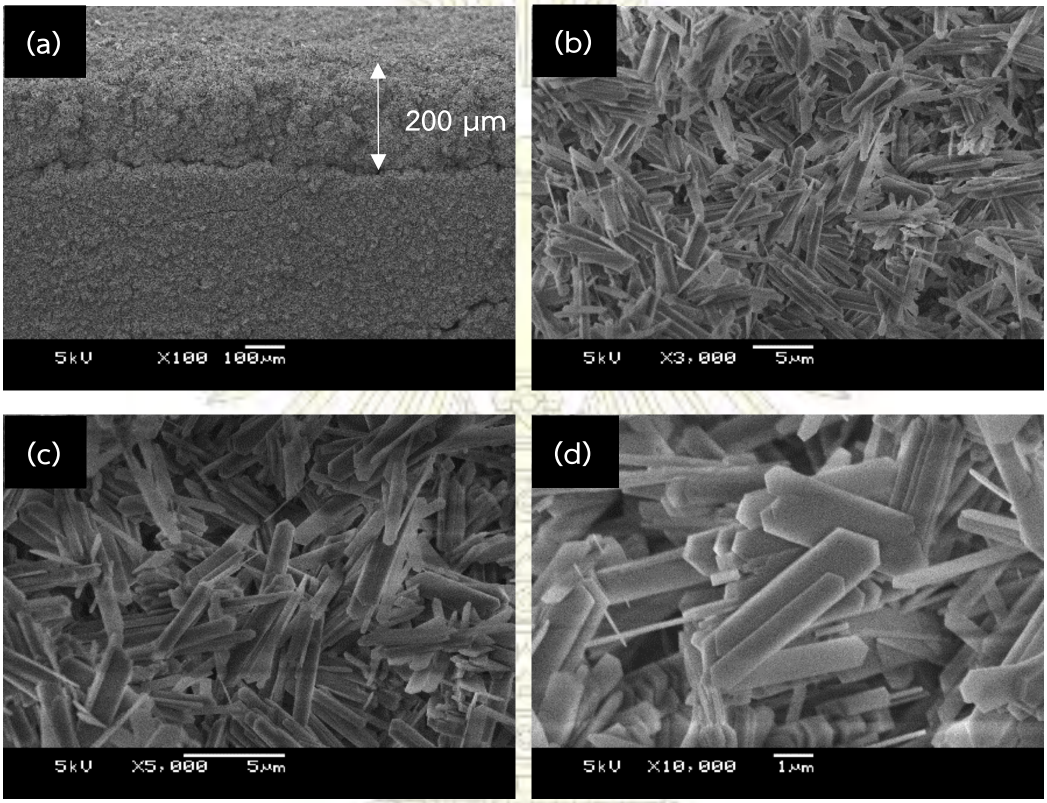


Figure 3.6 Scanning electron micrographs of Fe-TS-1 on silicon substrates (a)-(b) cross-section; (c)-(d) top view.

3.1.2 Nitrogen adsorption-desorption isotherms

Nitrogen adsorption-desorption isotherms of each materials are shown in Figure 3.8. When pressure increases initially, the adsorption also increase due to the volume filling into the pore. The nitrogen adsorption-desorption isotherms of all materials indicated type I isotherm which referred to the microporous materials according to the IUPAC classification and their textural properties are shown in Table 3.1. BET specific surface area of Fe-TS-1 is higher than that of TS-1 thin film because of the existence of Fe_2O_3 particles on the surface of the thin film and particle size of iron-titanium silicalite-1 is smaller than that of TS-1.

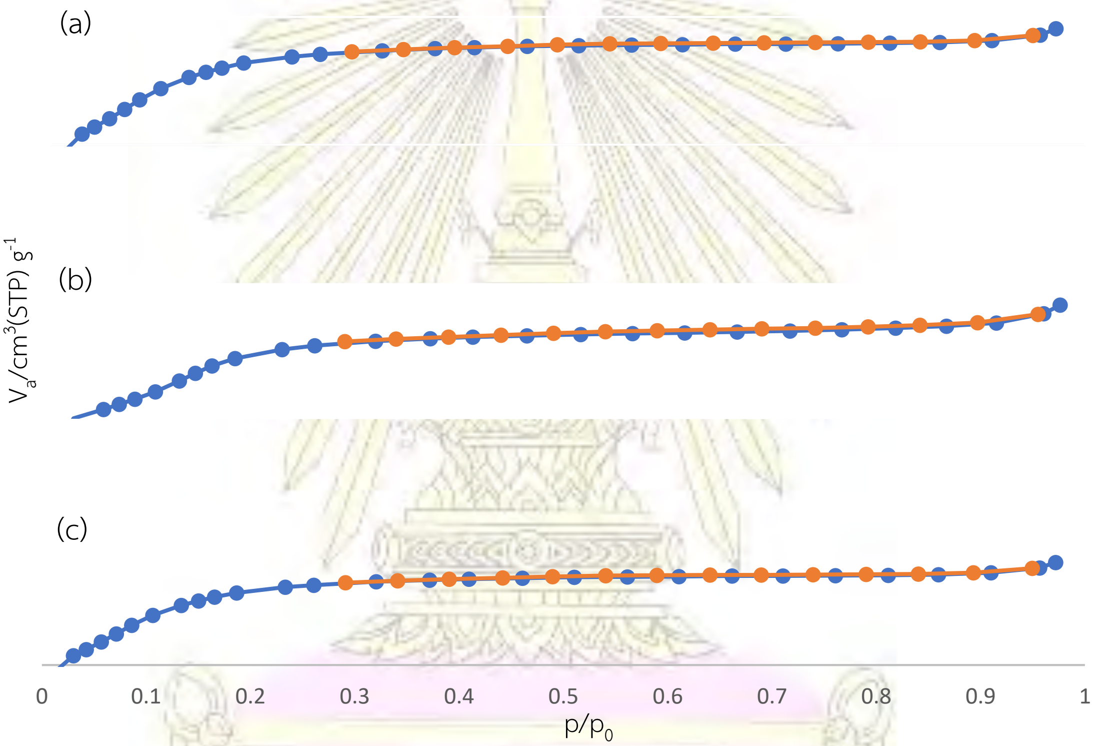


Figure 3.7 Nitrogen adsorption-desorption isotherms of thin film materials (a) Fe-TS-1 on silicon substrates; (b) TS-1 on silicon substrates; (c) TS-1 on silicon nanowires substrates.

Table 3.1 Textural properties of thin film catalysts.

catalyst	BET surface area (m^2g^{-1}) [a]	External surface area (m^2g^{-1}) [b]	Total pore volume (cm^3g^{-1}) [c]	Average pore diameter (nm) [c]
Titanium silicalite-1 on silicon substrates	313	4.0	0.13	0.7
Titanium silicalite-1 on silicon nanowire substrates	202	3.1	0.08	0.7
Iron-titanium silicalite-1 on silicon substrates	1406	5.1	0.57	0.7

[a] Reported by BET method

[b] Reported by t-plot

[c] Reported by MP plot

3.1.3 X-ray diffraction

From the X-ray diffractograms of iron-titanium silicaite-1 and titanium silicalite-1 on silicon and silicon nanowires substrates. Figure 3.8 shows the typical characteristic peaks of MFI structure.

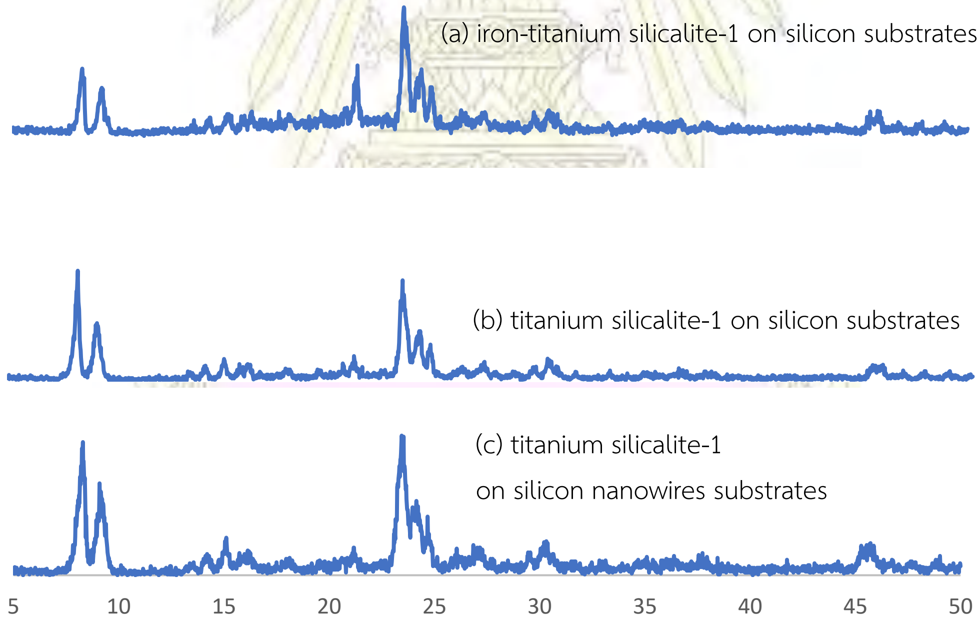


Figure 3.8 X-ray diffractograms of thin film catalysts (a) iron-titanium silicalite-1 on silicon substrates ;(b) titanium silicalite-1 on silicon substrates; (c) titanium silicalite-1 on silicon nanowires substrates

3.1.4 Elemental analysis

The catalysts were analyzed by SEM-EDS technique. The results are shown in Table 3.2. The mole ratio of Si/Ti in thin film catalyst was higher than initial gel because Ti was not fully incorporated to the framework. For Fe-TS-1 thin film, the mole ratio of Si/Fe was also higher than initial gel.

Table 3.2 Mole ratio of different catalysts.

catalyst	mole ratio in initial gel[a]		mole ratio in thin film catalyst[b]	
	Si/Ti	Si/Fe	Si/Ti	Si/Fe
TS-1 on silicon substrate	25	-	47	-
TS-1 on silicon nanowires substrates	25	-	32	-
Fe-TS-1 on silicon substrate	25	100	46	142

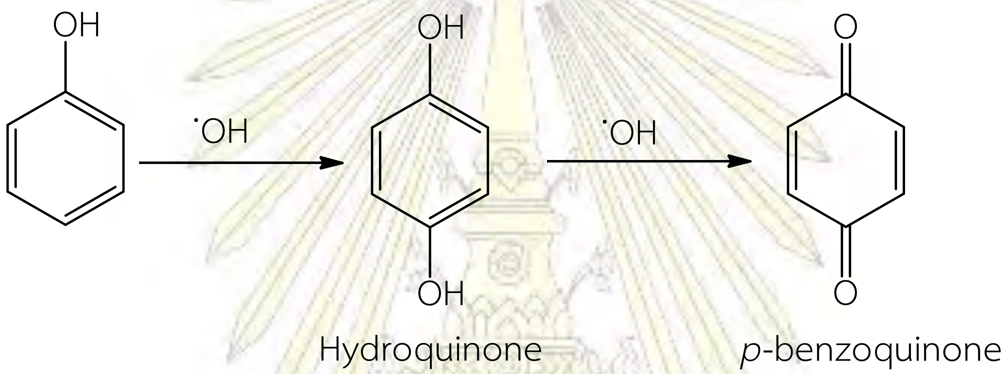
[a] Calculated from initial gel

[b] Determined by SEM-EDS

3.2 Catalytic activity of titanium silicalite-1 thin films

3.2.1 Catalytic activity of titanium silicalite-1 thin films on silicon substrates

Figures 3.10 and 3.11 shows the catalytic performance of titanium silicalite-1 on silicon substrates. It was found that the phenol conversion tends to decrease with time. The average of phenol conversion is 85.9 %. The overall of oxidation yield product rose slightly in the first 12 hours and remained constant until 48 hours. The average total oxidation product is 35.9 %. Hydroquinone achieved the highest yield and selectivity. The average yield and selectivity are 18.5 % and 54.2 %, respectively. The yield and selectivity of benzoquinone is slightly increasing after 30 hour because benzoquinone occurred after the oxidation of hydroquinone from Scheme 3.1.



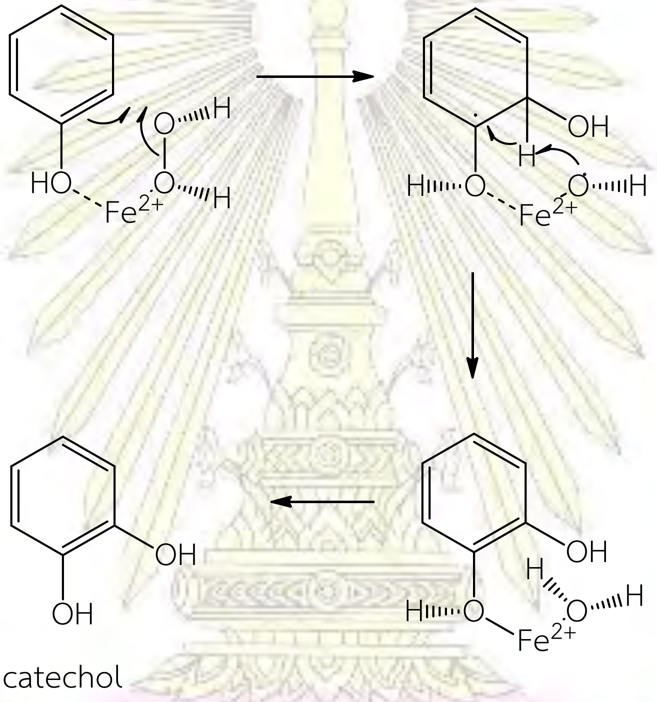
Scheme 3.1 oxidation of phenol and hydroquinone formation.

3.2.2 Catalytic activity of titanium silicalite-1 thin films on silicon nanowires substrates

From Figures 3.10 and 3.11, the catalytic performance of titanium silicalite-1 on silicon nanowires thin film shows the results that the phenol conversion is decreased with the passing of time. The average of phenol conversion is 86.2 %. The overall oxidation products are 39.35 %. Hydroquinone still gives the highest yield and selectivity of 22.8 % and 58.6 %, respectively. Catechol achieved 12.7 % of yield and 32.2 % of selectivity and benzoquinone gave yield 3.8 % and selectivity 9.2 %.

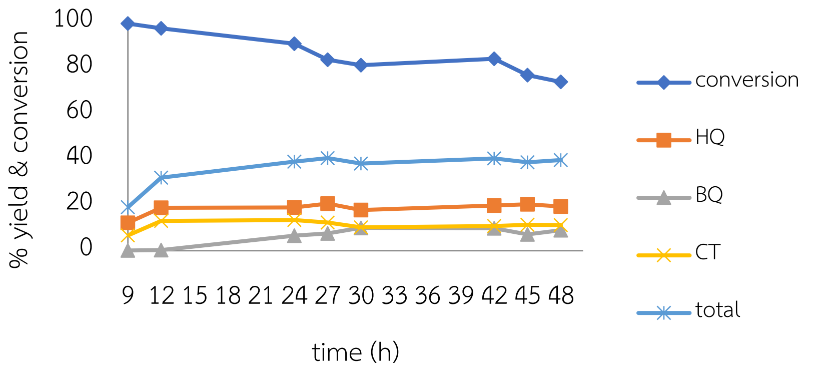
3.2.3 Catalytic activity of iron-titanium silicalite-1 thin films on silicon substrates

Figures 3.10 and 3.11 show that iron-titanium silicalite-1 gave lower phenol conversion and total oxidation products. This might be caused by the film thickness. Iron-titanium silicalite-1 film which deposited on silicon substrates is thinner than titanium silicalite-1. So, the mass of thicker film is higher and could promote the catalytic activity. Moreover, iron-titanium silicalite-1 obtained larger crystal size so it is quite more difficult to diffuse of the reactant molecule to the active site. On the other hand, the selectivity of catechol is higher than titanium silicalite-1 which undergo by the Fenton's reagent[32] which can be seen in scheme 3.2. Hydrogen peroxide was oxidized by ferrous ion and give hydroxy radical to react with phenol to produce catechol.

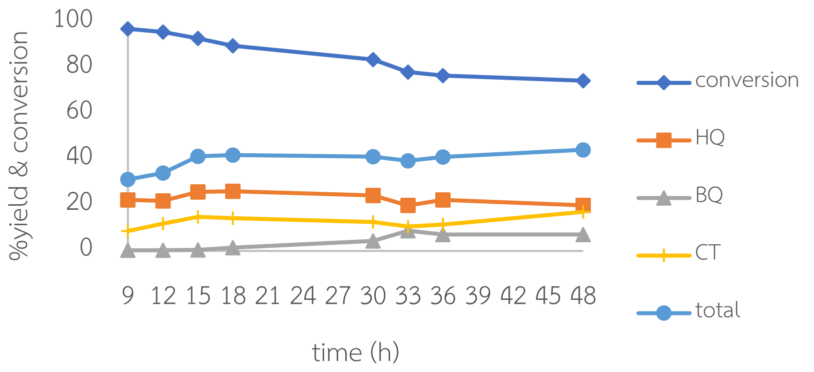


Scheme 3.2 Fenton's mechanism for oxidation of phenol to catechol.

(a) % yield & conversion in continuous flow reactor



(b) % yield & conversion in continuous flow reactor



(c) % yield & conversion in continuous flow reactor

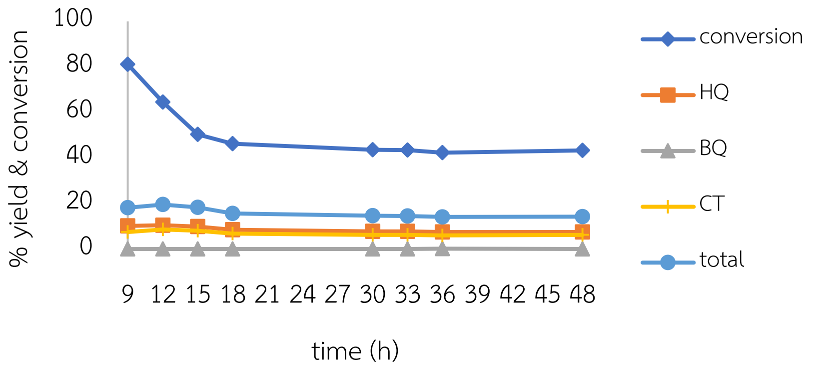
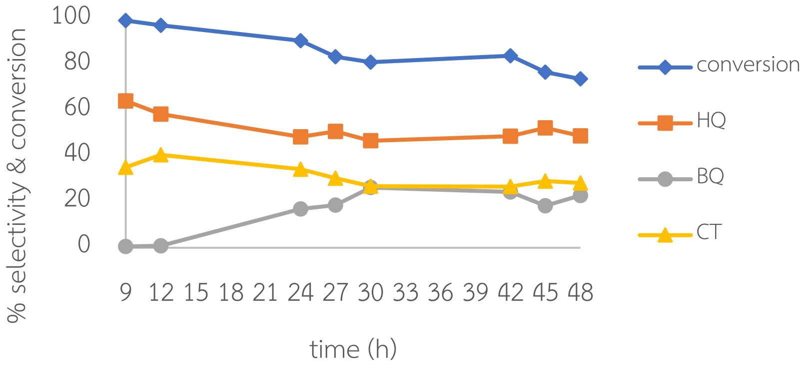
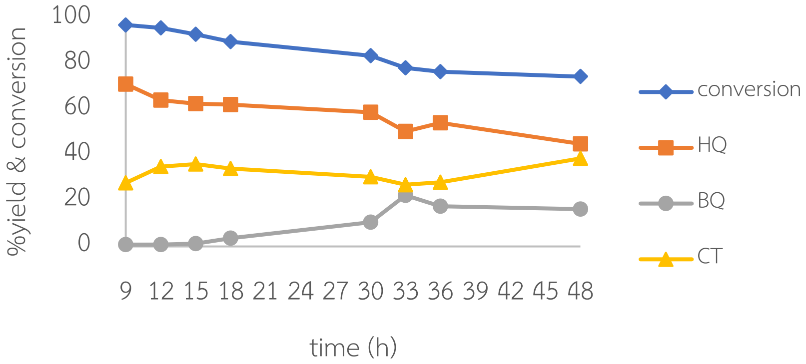


Figure 3.9 %yield and conversion for the phenol hydroxylation with catalysts (a) TS-1 on silicon substrates; (b) TS-1 on silicon nanowires substrates; (c) Fe-TS-1 on silicon substrates.

(a) % selectivity & conversion in continuous flow reactor



(b) % selectivity & conversion in continuous flow reactor



(c) % selectivity & conversion in continuous flow reactor

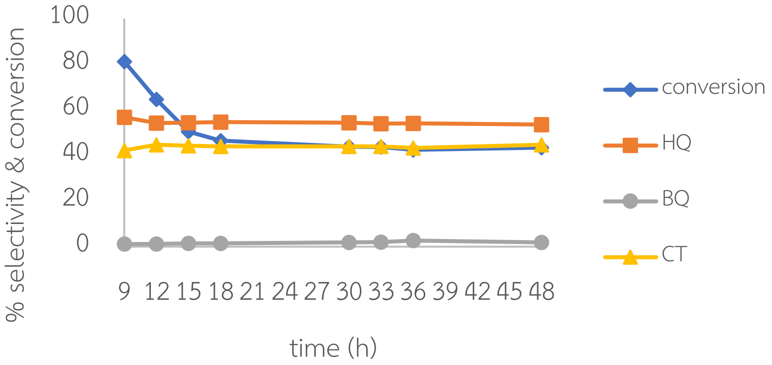


Figure 3.10 %selectivity and conversion for the phenol hydroxylation with catalysts (a) TS-1 on silicon substrates; (b) TS-1 on silicon nanowires substrates; (c) Fe-TS-1 on silicon substrates.

Table 3.3 comparison of phenol conversion and %yield over TS-1 thin film.

Catalyst	%phenol conversion	% yield			%total yield
		HQ	BQ	CT	
TS-1 on silicon substrates	85.88	18.48	0.11	6.69	35.94
TS-1 on silicon nanowires substrates	86.15	22.83	3.78	12.74	39.35
Fe- TS-1 on silicon substrates	51.98	8.88	0.27	7.15	16.30

Titanium silicalite-1 thin film on silicon nanowire substrates gave the highest yield of hydroquinone, benzoquinone and total oxidation products. The total oxidation products are not that much due to the coke formation from the over oxidation.

Table 3.4 comparison of phenol conversion and selectivity over TS-1 thin film in various types of flow reactors.

Catalyst	Condition	%Phenol conversion	%Selectivity		
			HQ	CT	BQ
TS-1 on Al_2O_3 tube[28]	phenol/H_2O_2 = 1:0.5 temperature = 85°C	10.2	95.6		-
TS-1 thin film on silicon substrate[33]	phenol/H_2O_2 = 1:2 temperature = 60°C	40.4	38.5	27.3	20.7
TS-1 wall microreactor[34]	phenol/H_2O_2 = 1:1.8 temperature = 60°C	44.6	98		-
Fe-ZSM-5 on stainless steel fiber[35]	phenol/H_2O_2 = 1:5 temperature = 80°C	95	45		-
TS-1 on silicon substrate (this work)	phenol/H_2O_2 = 1:2 temperature = 60°C	85.9	52.4	35.2	16.1
TS-1 on silicon nanowires substrate (this work)	phenol/H_2O_2 = 1:2 temperature = 60°C	86.1	58.6	32.2	9.2
Fe-TS-1 on silicon substrate (this work)	phenol/H_2O_2 = 1:2 temperature = 60°C	52.0	54.5	43.9	1.7

Table 3.2 shows the results for the catalytic performance of this work, compared to the previous studies of titanium silicalite-1 thin films in various types of reactor with these works. Fe-

ZSM-5 membrane give the highest %phenol conversion because this reaction was generated at high temperature. However, this work was carried out at lower temperature which caused fewer by-products and achieve high selectivity of oxidation products. Titanium silicalite-1 on wall reactor also give high selectivity because catalysts was packed on the wall of microreactor so it obtained higher amount of catalysts but lower phenol conversion than this work Although, phenol conversion on titanium silicalite-1 on Al_2O_3 tube was low due to the thinner of film., remind that the phenol conversion and selectivity also depend on the ratio of phenol/hydrogen peroxide and temperature.

CHAPTER V

CONCLUSION

Silicon nanowires substrates were successfully prepared by using metal-catalyzed electroless etching (MCEE) method. According to SEM micrographs, the average length of vertical silicon nanowires arrays was linearly increased with etching time within the range of 0-30 minutes.

Titanium silicalite-1 thin film was successfully synthesized by seeding and hydrothermal method on silicon nanowires substrates. The films showed good crystallinity of MFI structure. SEM micrographs displayed uniform blade-liked crystals. The nitrogen absorption-desorption demonstrated Type-I isotherm, which indicates the microporous structure. The continuous flow reaction showed high phenol conversion and selectivity.

Furthermore, the loading of iron into the initial gel of titanium silicalite-1 also showed the good crystallinity of MFI structure and microporous structure. The phenol conversion was decreased comparing to the titanium silicalite-1 without metal-loading but it gave higher selectivity of catechol.

REFERENCES

1 Lerner, L. 7 things you may not know about catalysis. http://www.anl.gov/articles/7-things-you-may-not-know-about-catalysis (accessed 10 April, 2017).

2 Matthey, J. Refinery (FCC, Hydrocracking, Catalytic Reforming), Synthesis, Polymer & Environmental Catalyst Market - Global Industry Analysis by Material (Zeolites, Metal, Others), by Type (Homogenous & Heterogeneous), Catalyst Regeneration (Off-site & On-site), Size, Share, Growth, Trends and Forecast 2012 - 2018. http://www.transparencymarketresearch.com/global-refinery-catalyst-market.html

3 Armor, J. N., A History of Industrial Catalysis. *Catal. Today* **2011,** *163*, 3-9.

4 Frei, H., Selective Hydrocarbon Oxidation in Zeolites. **2006,** *5785*, 309-310.

5 Barbera, D.; Cavani, F.; D'Alessandro, T.; Fornasari, G.; Guidetti, S.; Aloise, A.; Giordano, G.; Piumetti, M.; Bonelli, B.; Zanzottera, C., The Control of Selectivity in Benzene Hydroxylation Catalyzed by TS-1: The Solvent Effect and the Role of Crystallite Size. *J. Catal.* **2010,** *275*, 158-169.

6 Yu, J.; Yang, P.; Yang, Y.; Wu, T.; Parquette, J. R., Hydroxylation of Phenol with Hydrogen Peroxide Over Tungstovanadophosphates with Dawson Structure. *Catal. Commun.* **2006,** *7*, 153-156.

7 Sahner, K.; Hagen, G.; Schonauer, D.; Reis, S.; Moos, R., Zeolites — Versatile Materials for Gas Sensors. *Solid State Ion.* **2008,** *179*, 2416-2423.

8 Ning, X.; Zhao, C. L.; Yang, J.; Chan, C. C., Zeolite Thin Film-Coated Spherical End-Face Fiber Sensors for Detection of Trace Organic Vapors. *Opt. Commun.* **2016,** *364*, 55-59.

9 Caro, J.; Noack, M., Zeolite membranes – Recent Developments and Progress. *Microporous Mesoporous Mater.* **2008,** *115*, 215-233.

10 Cha, J. L. H.; Wan, Y. S. S.; Gavriilidis, A.; Yeung, K. L., Incorporating Zeolites in Microchemical Systems. *Chem. Eng. J.* **2002,** *88*, 187-200.

11 Yilmaz, B.; Müller, U., Catalytic Applications of Zeolites in Chemical Industry. *Top. Catal.* **2009,** *52*, 888-895.

12 Kaucic, V., The Structure of Zeolite and Aluminophosphase Molecular Seive. *Croat. Chem. Acta.* **1994,** *67*, 241-261.

13 Hizmetleri, B. T., Zeolite (Clinoptiolite). http://www.gordeszeolite.com/zeolite--clinoptilolite-(accessed 15 April, 2017).

14 Karmen Margeta, N. a. Z. L., Mario Šiljeg and Anamarija Farkas Natural Zeolites in Water Treatment – How Effective is Their Use, Water Treatment.

https://www.intechopen.com/books/water-treatment/natural-zeolites-in-water-treatment-how-effective-is-their-use (accessed 15 April, 2017).

15 Locke, W. Zeolites. http://www.ch.ic.ac.uk/vchemlib/course/zeolite/structure.html (accessed 15 April, 2017).

16 Li, J.; Corma, A.; Yu, J., Synthesis of New Zeolite Structures. *Chem Soc Rev.* **2015,** *44*, 7112-7127.

17 Saxton, R. J., Crystalline Microporous Titanium Silicates. *Top. Catal.* **1999,** *9*, 43-57.

18 Zhang, H.; Liu, Y.; Jiao, Z.; He, M.; Wu, P., Hydrothermal Synthesis of Titanium Silicalite-1 Structurally Directed by Hexamethyleneimine. *Ind. Eng. Chem. Res.* **2009,** *48*, 4334–4339.

19 Meng, L.; Guo, H.; Dong, Z.; Jiang, H.; Xing, W.; Jin, W., Ceramic Hollow Fiber Membrane Distributor for Heterogeneous Catalysis: Effects of Membrane Structure and Operating Conditions. *Chem. Eng. J.* **2013,** *223*, 356-363.

20 Choi, J. S.; Yoon, S. S.; Jang, S. H.; Ahn, W. S., Phenol Hydroxylation Using Fe-MCM-41 Catalysts. *Catal. Today* **2006,** *111*, 280-287.

21 Wróblewska, A., Water as the Solvent for the Process of Phenol Hydroxylation Over the Ti-MWW Catalyst. *React. Kinet., Mech. Catal.* **2012,** *108*, 491-505.

22 Wilkenhöner, U.; Langhendries, G.; van Laar, F.; Baron, G. V.; Gammon, D. W.; Jacobs, P. A.; van Steen, E., Influence of Pore and Crystal Size of Crystalline Titanosilicates on Phenol Hydroxylation in Different Solvents. *J. Catal.* **2001,** *203*, 201-212.

23 Hu, Y.; Peng, K. Q.; Qiao, Z.; Huang, X.; Zhang, F. Q.; Sun, R. N.; Meng, X. M.; Lee, S. T., Metal-Catalyzed Electroless Etching of Silicon in Aerated HF/H_2O Vapor for Facile Fabrication of Silicon Nanostructures. *Nano Lett* **2014,** *14*, 4212-9.

24 Taramasso, M.; Perego, G.; Notari, B., Preparation of Porous Crystalline Synthetic Material Comprised of Silicon and Titanium Oxides. Google Patents: 1983.

25 Zhang, J. H.; Yue, M. B.; Wang, X. N.; Qin, D., Synthesis of Nanosized TS-1 Zeolites Through Solid Transformation Method with Unprecedented Low Usage of Tetrapropylammonium Hydroxide. *Microporous Mesoporous Mater.* **2015,** *217*, 96-101.

26 Zuo, Y.; Wang, X.; Guo, X., Synthesis of Titanium Silicalite-1 with Small Crystal Size by Using Mother Liquid of Titanium Silicalite-1 As Seed. *Ind. Eng. Chem. Res.* **2011,** *50*, 8485-8491.

27 Qiu, F.; Wang, X.; Zhang, X.; Liu, H.; Liu, S.; Yeung, K. L., Preparation and Properties of TS-1 Zeolite and Film Using Sil-1 Nanoparticles as Seeds. *Chem. Eng. J.* **2009,** *147*, 316-322.

28 Wang, X.; Zhang, X.; Liu, H.; Yeung, K. L.; Wang, J., Preparation of Titanium Silicalite-1 Catalytic Films and Application as Catalytic Membrane Reactors. *Chem. Eng. J.* **2010,** *156*, 562-570.

29 Wu, M.; Chou, L.; Song, H., Effect of Metals on Titanium Silicalite TS-1 for Butadiene Epoxidation. *Chin. J. Catal.* **2013,** *34*, 789-797.

30 Wan, Y., 1-Pentene Epoxidation in Catalytic Microfabricated Reactors. *J. Catal.* **2004,** *223*, 241-249.

31 Phansa, C. Silicon Nanowires (SiNWs) Syntheses and Characteristics of SiNWs-based Solar Cells.Dissertation, Chulalongkorn University, 2015.

32 Esther, L. P. M.; Revathi, S.; Sivakumar, T.; Manikandan, D.; Divakar, D.; Valentine Rupa, A.; Palanichami, M., Phenol Hydroxylation Using Fe/Al-MCM-41 Catalysts. *Catal. Lett.* **2007,** *120*, 56-64.

33 Sriyanai, K. Titanosilicate Porous Thin Film on Silicon Substrate as Catalyst for Hydroxylation of Phenol in Continuous Flow Reactor. Dissertation, Chulalongkorn Univetsity, 2016.

34 Yube, K.; Furuta, M.; Mae, K., Selective Oxidation of Phenol with Hydrogen Peroxide Using Two Types of Catalytic Microreactor. *Catal. Today* **2007,** *125*, 56-63.

35 Yan, Y.; Jiang, S.; Zhang, H.; Zhang, X., Preparation of Novel Fe-Zsm-5 Zeolite Membrane Catalysts for Catalytic Wet Peroxide Oxidation Of Phenol in a Membrane Reactor. *Chem. Eng. J.* **2015,** *259*, 243-251.

APPENDICES

1. Calculation of %conversion of reactant and selectivity of products

$$\&\text{conversion} = \frac{\text{Reacted mole of phenol}}{\text{Initial mole of phenol}} \times 100$$

$$\&\text{selectivity to hydroquinone} = \frac{\text{mole of hydroquinone}}{\text{total mole of all products}} \times 100$$

$$\&\text{selectivity to catechol} = \frac{\text{mole of catechol}}{\text{total mole of all products}} \times 100$$

$$\&\text{selectivity to benzoquinone} = \frac{\text{mole of benzoquinone}}{\text{total mole of all products}} \times 100$$

2. Calibration calculation

2.1 Phenol calibration curve

The standard curve of equation is expressed as following

$$y = 0.8707x - 0.1482$$

where y is M_{Ph}/M_{Isd}; M_{Ph} = mass of phenol (g)

M_{Isd} = mass of internal standard (cycloheptanone, g)

x is A_{Ph}/A_{Isd}; A_{Ph} = peak area of phenol

A_{Isd} = peak area of internal standard

The correlation coefficient R^2 value for phenol calibration curve is 0.9947.

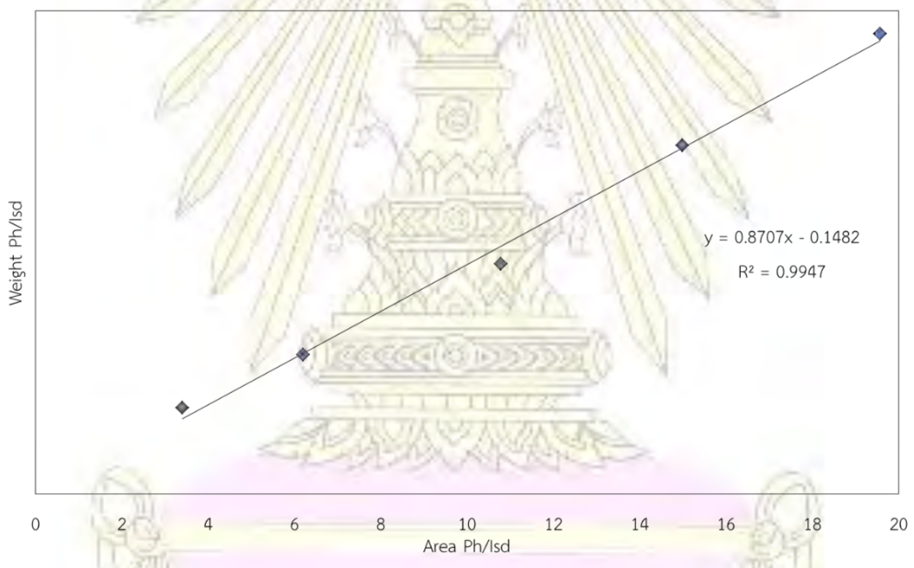


Figure A-1 Calibration curve of phenol.

2.2 Hydroquinone calibration curve

The standard curve of equation is expressed as following

$$y = 0.7632x + 0.1807$$

where y is M_{HQ}/M_{Isd}; M_{HQ} = mass of hydroquinone (g)

M_{Isd} = mass of internal standard (cycloheptanone, g)

x is A_{HQ}/A_{Isd}; A_{HQ} = peak area of hydroquinone

A_{Isd} = peak area of internal standard

The correlation coefficient R^2 value for hydroquinone calibration curve is 0.999.

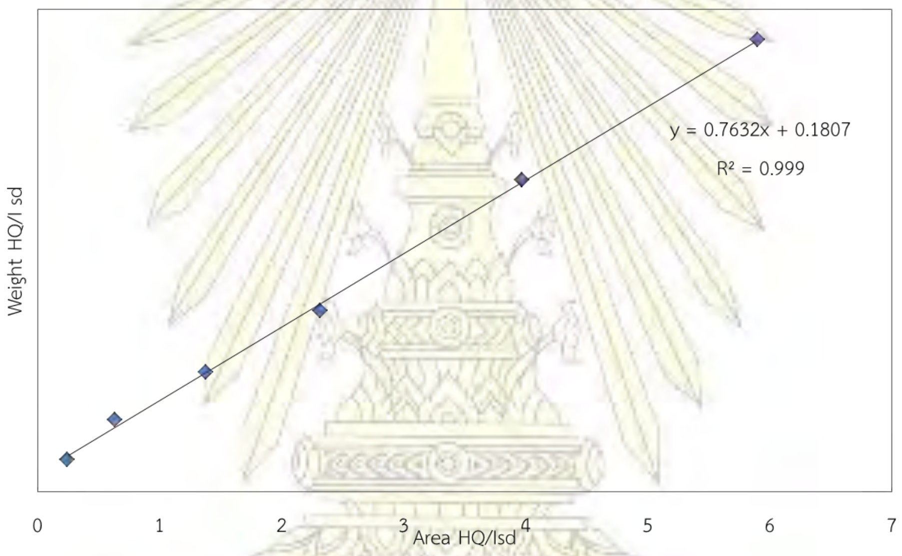


Figure A- 2 Calibration curve of hydroquinone.

2.3 Catechol calibration curve

The standard curve of equation is expressed as following

$$y = 0.7312x + 0.1113$$

where y is M_{CT}/M_{Isd}; M_{CT} = mass of catechol (g)

M_{Isd} = mass of internal standard (cycloheptanone, g)

x is A_{CT}/A_{Isd}; A_{CT} = peak area of catechol

A_{Isd} = peak area of internal standard

The correlation coefficient R^2 value for catechol calibration curve is 0.9993.

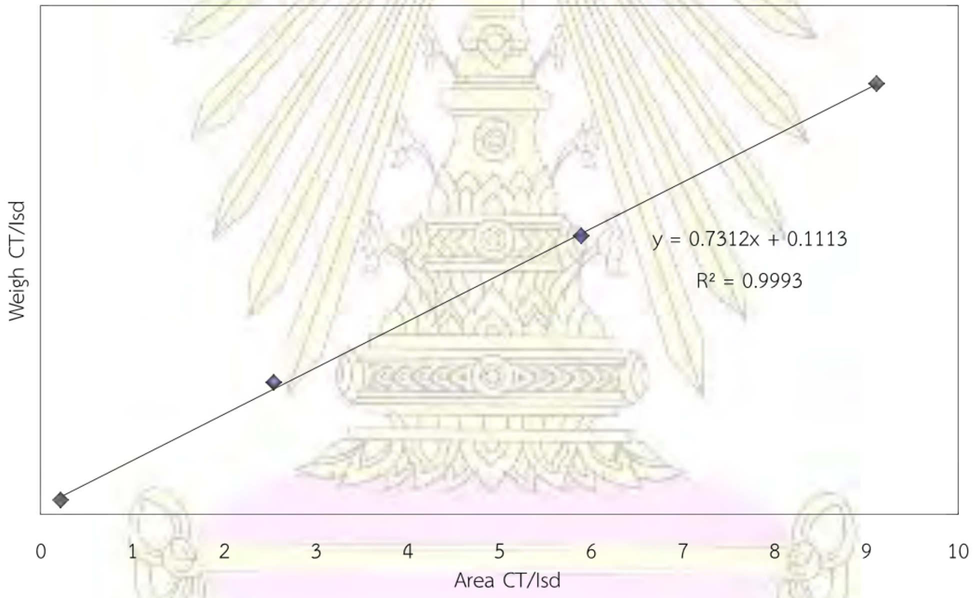


Figure A- 3 Calibration curve of catechol.

2.4 Benzoquinone calibration curve

The standard curve of equation is expressed as following

$$y = 1.1257x + 0.0053$$

where y is M_{BQ}/M_{Isd}; M_{BQ} = mass of benzoquinone (g)

M_{Isd} = mass of internal standard (cycloheptanone, g)

x is A_{HQ}/A_{Isd}; A_{HQ} = peak area of benzoquinone

A_{Isd} = peak area of internal standard

The correlation coefficient R^2 value for benzoquinone calibration curve is 0.9994.

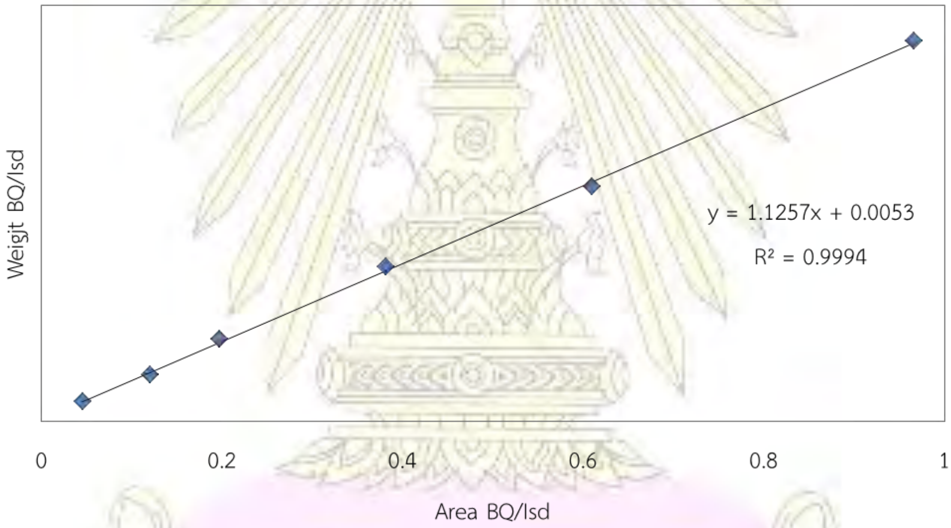


Figure A- 4 Calibration curve of benzoquinone.

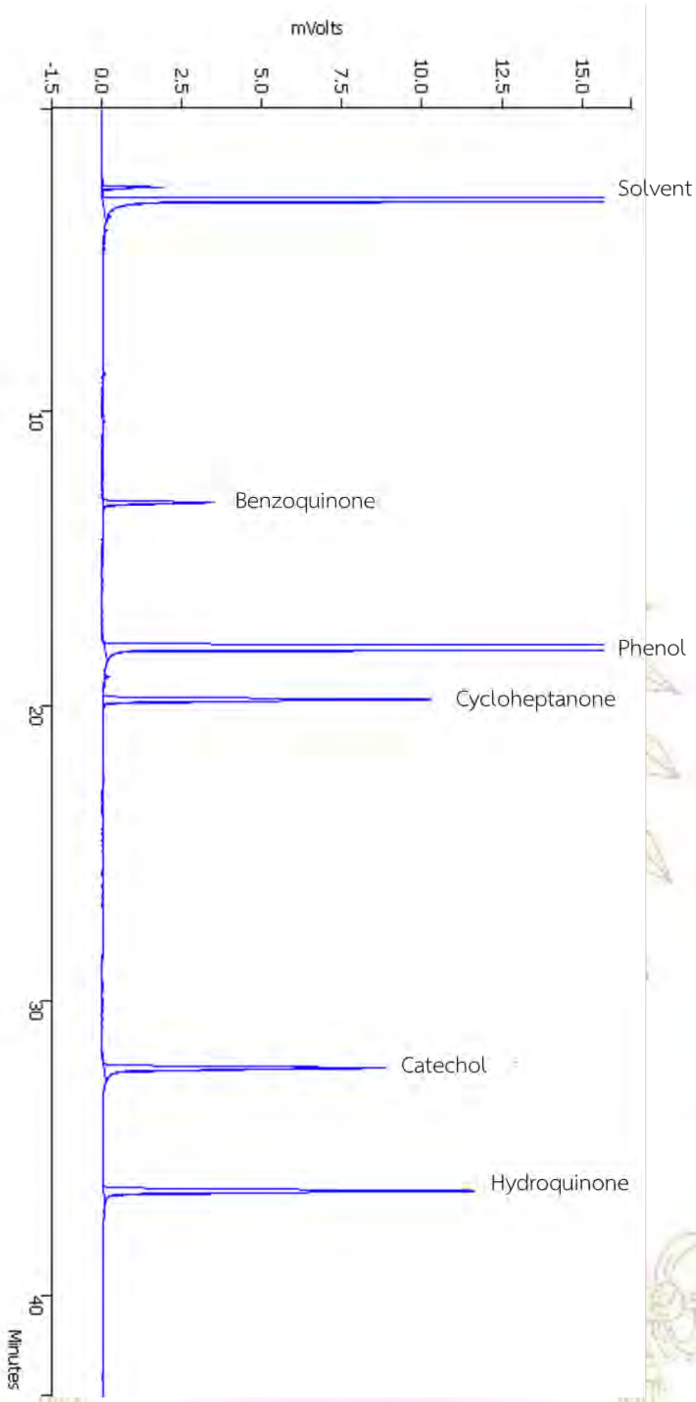


Figure A- 5 GC chromatogram of products from phenol hydroxylation using the cycloheptanone as solvent and cycloheptanone as internal standard.

VITA

Mr. Peerat Malineekul was born on September, 8th, 1993 in Lampang, Thailand. He graduated high school from Bunyawat Wittayalai school, Lampang. in 2012. He has been studied a Bachelor Degree of Science in Department of Chemistry, Faculty of Science, Chulalongkorn University in 2013. His address is 138 M.12, Jamtawee Road, Bohaew Sub-district, Muang District, Lampang, 52100. E-mail: malineekul123@hotmail.com