

# SYNTHESIS AND ACTIVITY OF Ti-Fe-SBA-15 FROM SILATRANE

Ratchadaporn Kaewmuang

A Thesis Submitted in Partial Fulfilment of the Requirements  
for the Degree of Master of Science  
The Petroleum and Petrochemical College, Chulalongkorn University  
in Academic Partnership with  
The University of Michigan, The University of Oklahoma,  
and Case Western Reserve University  
2014

I 2637 0521

570093

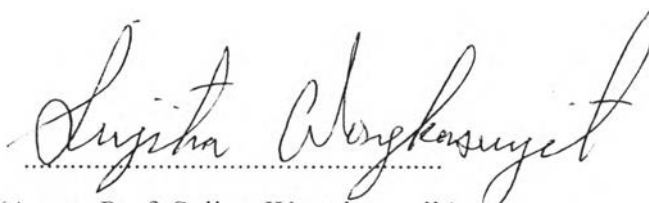
**Thesis Title:** Synthesis and Activity of Ti-Fe-SBA-15 from Silatrane  
**By:** Ratchadaporn Kaewmuang  
**Program:** Polymer Science  
**Thesis Advisors:** Assoc. Prof. Sujitra Wongkasemjit  
Asst. Prof. Thanyalak Chaisuwan

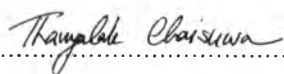
---


Accepted by The Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.


  
..... College Dean  
(Asst. Prof. Pomthong Malakul)

**Thesis Committee:**

  
.....  
(Assoc. Prof. Sujitra Wongkasemjit)

  
.....  
(Asst. Prof. Thanyalak Chaisuwan)

  
.....  
(Asst. Prof. Hathaikarn Manuspiya)

  
.....  
(Asst. Prof. Bussarin Ksapabutr)

**ABSTRACT**

5572018063: Polymer Science Program

Ratchadaporn Kaewmuang: Synthesis and Activity of Ti-Fe-SBA-15 from Silatrane.

Thesis Advisors: Assoc. Prof. Sujitra Wongkasemjit and Asst. Prof. Thanyalak Chaisuwan 78 pp.

Keywords: Silatrane/ SBA-15/ Bimetallic/ Iron/ Titanium/ Phenol hydroxylation/ Sol-gel process

Monomeric- and bimetallic-incorporated SBA-15 (Fe-SBA-15, Ti-SBA-15 and 0.01Fe-0.01Ti-SBA-15) were successfully synthesized via sol gel process at room temperature in highly acidic condition using silatrane, ferric chloride and titanium isopropoxide as a silica, iron, and titanium sources, respectively, Pluronic 123 as template. It was found that from SAXS patterns and Fe-SEM images all samples maintained their 2D hexagonal mesoporous structure. The result from N<sub>2</sub> adsorption-desorption measurement showed type (IV) isotherm with H1 hysteresis loop and uniform pores as well as high surface area (631–763 m<sup>2</sup>/g), pore volume (0.621-0.971 cc/g), and large pore size (3.93–5.21 nm). DR-UV spectra confirmed the metal incorporation with no extraframework. Its catalytic activity was studied for phenol hydroxylation using H<sub>2</sub>O<sub>2</sub> as oxidizing agent and showed that the highest phenol conversion at 37.96% with 100% selectivity of benzoquinone was obtained when using 1:1 molar ratio of phenol/H<sub>2</sub>O<sub>2</sub> and 30 mg of 0.01Fe-0.01Ti-SBA-15 at 30 °C for 20 min.

## บทคัดย่อ

รัชดาภรณ์ แก้วเมือง: ศึกษาการสังเคราะห์และการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยา Ti-Fe-SBA-15 จากไซลาเทรน (Synthesis and Activity of Ti-Fe-SBA-15 from Silatrane) อาจารย์ที่ปรึกษา: รศ.ดร. สุจิตรา วงศ์เกษมจิตต์ และ ผศ.ดร. ธัญลักษณ์ ฉายสุวรรณ 78 หน้า

ตัวรองรับซิลิกาชนิด SBA-15 ที่มีการเติมโลหะเดี่ยวและโลหะผสม (Fe-SBA-15, Ti-SBA-15 and 0.01Fe-0.01Ti-SBA-15) สามารถสังเคราะห์ได้ผลอย่างดี โดยใช้กระบวนการโซลเจลที่อุณหภูมิห้องในสภาวะที่เป็นกรดแก่ ซึ่งใช้ไซลาเทรน, เพอร์ริคคลอไรด์, และไททานเนียมไอโซโพรพอกไซด์ เป็นแหล่งของซิลิกา, เหล็กและไททานเนียม ตามลำดับ, ใช้พลูโรนิค 123 เป็นตัวแม่แบบ จากการวิเคราะห์ด้วยเครื่องมือ เอ็กซ์เรย์สแกตเตอร์รังสีชนิดสมอลแองเกิล (SAXS) และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (FESEM) พบว่า สารที่สังเคราะห์ได้ทุกตัวนั้นสามารถรักษาโครงสร้างที่มีรูพรุนขนาดกลางแบบหกเหลี่ยมสองมิติได้ และจากการวิเคราะห์ด้วยการดูดซับและการคายของก๊าซไนโตรเจนพบว่า สารที่สังเคราะห์ได้นั้นจัดอยู่ในไอโซเทอมประเภทที่สี่ ชนิดเฮชหนึ่ง ซึ่งมีรูพรุนที่สม่ำเสมอ และมีพื้นที่ผิวสูง (631-763 ตารางเมตรต่อกรัม) โดยมีปริมาตรของรูพรุนที่สูง (0.621-0.971 ลูกบาศก์เซนติเมตรต่อกรัม) และมีรูพรุนขนาดใหญ่ (3.93-5.21 นาโนเมตร) ผลจากการวิเคราะห์ด้วยเครื่อง DR-UV ยืนยันได้ว่ามีโลหะอยู่เฉพาะแต่ในโครงสร้างของตัวรองรับ SBA-15 จากการศึกษาผลของการเร่งปฏิกิริยาฟินอลไฮดร็อกซีเลชัน โดยใช้ไฮโดรเจนเปอร์ออกไซด์เป็นตัวออกซิเด้นท์ นั้น พบว่า สารรองรับ SBA-15 ที่มีการเติมโลหะผสม (0.01Fe-0.01Ti-SBA-15) สามารถเปลี่ยนฟินอลเป็นผลิตภัณฑ์ได้มากที่สุดถึง 37.96 เปอร์เซ็นต์ โดยมีความสามารถในการเลือกจำเพาะของเบนโซควิโนนถึง 100 เปอร์เซ็นต์ เมื่อใช้ตัวเร่งนี้ในปริมาณ 30 มิลลิกรัม ทำปฏิกิริยาที่อุณหภูมิ 30 องศาเซลเซียส เป็นเวลา 20 นาที และใช้อัตราส่วนโดยโมลต่อลิตรระหว่างฟินอลต่อไฮโดรเจนเปอร์ออกไซด์ที่หนึ่งต่อหนึ่ง

## ACKNOWLEDGMENTS

First of all, I would like to thank to my advisor, Assoc. Prof. Sujitra Wongkasemjit, who not only gave me a great opportunity to do a challenging research about the catalyst, but also taught me how to manage myself for solving the problem in the real situation. I would have not succeeded if I do not have her motivation, understanding, good advice, trusting in me and precious encouragement when I was in a big trouble. I really appreciate it and it will be one of my best memories in my life. Moreover, I would like to give special thanks to Asst. Prof. Thanyalak Chaisuwan, my co-adviser, Asst. Prof. Hathaikarn Manuspiya, and Asst. Prof. Bussarin Ksapabutr for kindly being dissertation committees, making valuable comments, and suggestions.

I am grateful for the scholarship and funding of the thesis work provided by The Petroleum and Petrochemical College; Chulalongkorn University; Thailand and The Center of Excellence on Petrochemical and Materials Technology, Thailand. All PPC's officers are appreciated for helping and facilitating me until I achieved this work.

I would like to thank all of my PPC's friends who continuously supported and encouraged me when I was in tough situations. I had the valuable and cheerful time when I worked with them.

Most of all, I would like to express my thankfulness to my family for their understanding, encouragement, support, limitless sacrifice, and advice, as always.

## TABLE OF CONTENTS

	<b>PAGE</b>
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	ix
List of Figures	x
 <b>CHAPTER</b>	
<b>I INTRODUCTION</b>	<b>1</b>
<b>II LITERATURE REVIEW</b>	<b>3</b>
2.1 Hydroxylation of Phenol	3
2.2 Hydroxylation of Phenol Using Titanium Containing Materials	6
2.2.1 Titanium Silicate-1 (TS-1)	6
2.2.2 Hydroxylation of Phenol Using Titanium on Mesoporous Materials	7
2.3 Hydroxylation of Phenol Using Iron Containing Mesoporous Materials	10
2.4 Hydroxylation of Phenol Using Bimetallic (Fe or Ti) Incorporated Materials	15
2.5 Mesoporous Materials	15
2.6 Introduction to SBA-15	16
2.6.1 SBA-15 Synthesis	17
2.6.2 Silatrane Precursor	19
2.6.3 Bimetallic Incorporated on SBA-15	21

<b>CHAPTER</b>		<b>PAGE</b>
<b>III</b>	<b>EXPERIMENTAL</b>	24
	3.1 Materials	24
	3.2 Materials Characterization	25
	3.3 Precursor Synthesis	27
	3.3.1 Silatrane Synthesis	27
	3.4 Catalyst Synthesis	28
	3.4.1 Synthesis of SBA-15	28
	3.4.2 Synthesis of Ti-SBA-15	28
	3.4.3 Synthesis of Fe-SBA-15	28
	3.4.4 Synthesis of Ti-Fe-SBA-15	29
	3.5 Catalytic Activity	29
	3.5.1 Phenol Hydroxylation Procedure	29
	3.5.2 Leaching and Reusability of the Catalyst	30
<b>IV</b>	<b>SYNTHESIS AND ACTIVITY OF Ti-Fe-SBA-15 FROM SILATRANE</b>	31
	4.1 Abstract	31
	4.2 Introduction	32
	4.3 Experimental	33
	4.3.1 Materials	33
	4.3.2 Precursor Synthesis	33
	4.3.3 Materials Characterization	35
	4.3.4 Phenol Hydroxylation Procedure	36
	4.3.5 Leaching and Reusability of the Catalyst	36
	4.4 Results and Discussion	37
	4.4.1 Characterization of Silatrane Precursor	37
	4.4.2 Characterization of Fe-SBA-15 Catalyst	38
	4.4.3 Characterization of Ti-SBA-15 Catalyst	44
	4.4.4 Characterization of Fe-Ti-SBA-15 Catalyst	48
	4.4.5 Catalytic Activity on Phenol Hydroxylation	51

<b>CHAPTER</b>	<b>PAGE</b>
4.5 Conclusions	62
4.6 Acknowledgments	62
4.7 References	62
<b>V CONCLUSIONS AND RECOMMENDATIONS</b>	<b>65</b>
5.1 Conclusions	65
5.2 Recommendations	65
<b>REFERENCES</b>	<b>66</b>
<b>APPENDICES</b>	<b>72</b>
<b>Appendix A</b> WAXD patterns of all catalysts	72
<b>Appendix B</b> Study on phenol hydroxylation	73
<b>CURRICULUM VITAE</b>	<b>78</b>



## LIST OF TABLES

TABLE		PAGE
2.1	Catalytic performance of different samples	8
2.2	FTIR Peak positions and assignments of the synthesized silatrane	21
2.3	Metal loading (wt%) of the calcined mono/bimetallic Co-Fe catalysts	23
4.1	BET surface area, pore volume, and average pore diameter of xFe- 15 samples	42
4.2	XRF data of Ti-SBA-15, Fe-SBA-15, and bimetallic Ti-Fe-SBA- 15	43
4.3	Effect of the metal loaded on phenol hydroxylation (Thermal reaction) at 30 °C for 20 min using 30 mg of catalyst and 1:1 phenol:H <sub>2</sub> O <sub>2</sub> ratio	55
4.4	Physical properties of the catalysts after used and calcined at 30 °C for 20 min using 30 mg of catalyst and 1:1 phenol:H <sub>2</sub> O <sub>2</sub> ratio	56
4.5	Study on the catalyst leaching of bimetallic 0.01Fe-0.01Ti-SBA- 15 at 30 °C for 20 min using 30 mg of 0.01Fe-0.01Ti-SBA-15 and 1:1 phenol:H <sub>2</sub> O <sub>2</sub> ratio	57
4.6	Study on the reusability of bimetallic 0.01Fe-0.01Ti-SBA-15 at 30 °C for 20 min using 30 mg of 0.01Fe-0.01Ti-SBA-15 and 1:1 phenol:H <sub>2</sub> O <sub>2</sub> ratio	58
B1	Effect of temperature and time on phenol hydroxylation (Thermal reaction)	73
B2	Effect of catalyst content on phenol hydroxylation (Thermal reaction)	75
B3	Effect of Molar ratio (phenol: H <sub>2</sub> O <sub>2</sub> ) on phenol hydroxylation (Thermal reaction)	75

## LIST OF FIGURES

FIGURE	PAGE
2.1	Chemical structures of: a) phenol, b) CAT, and c) HQ. <span style="float: right;">3</span>
2.2	Radical mechanism of hydroxylation of phenol by H <sub>2</sub> O <sub>2</sub> . <span style="float: right;">4</span>
2.3	The formation of CAT and HQ via electrophilic aromatic substitution mechanism. <span style="float: right;">5</span>
2.4	Reaction pathway for the phenol electro-catalytic oxidation on mixed metal oxides. <span style="float: right;">5</span>
2.5	SEM micrographs of TS-1 synthesized with amorphous SiO <sub>2</sub> (1), colloidal silica (2), and TEOS (3). <span style="float: right;">7</span>
2.6	Schematic diagram of hydroxylation of phenol with H <sub>2</sub> O <sub>2</sub> and tar formation. <span style="float: right;">9</span>
2.7	The oxidation of substituted phenols using Ti-HMA at room temperature. <span style="float: right;">9</span>
2.8	The catalytic cycle of the phenol oxidation by H <sub>2</sub> O <sub>2</sub> in the presence of RH-10Fe. <span style="float: right;">11</span>
2.9	Catalyst recycling effect on the phenol conversions at 50 °C using 1:1 phenol:H <sub>2</sub> O <sub>2</sub> in water over Fe-MCM-41 calcined at 550 °C; (▲) first cycle (4 mol%), (●) second cycle (2.8 mol%), (■) third cycle (2.5 mol%) (Fe/Si measured by SEM-EDS). <span style="float: right;">12</span>
2.10	Phenol hydroxylation reaction pathway of Fe ions. <span style="float: right;">13</span>
2.11	Proposed mechanism of phenol oxidation with H <sub>2</sub> O <sub>2</sub> over Fe-VSB-5. <span style="float: right;">14</span>
2.12	a) SEM and b) TEM of SBA-15. <span style="float: right;">16</span>
2.13	The mechanism of SBA-n formation. <span style="float: right;">18</span>
2.14	Preparation of silatrane precursor. <span style="float: right;">20</span>
2.15	XRD pattern of silatrane. <span style="float: right;">21</span>

FIGURE	PAGE
2.16 X-rays diffraction patterns recorded for the HMS (left) and SBA-15 (right) support and mono/bimetallic Co/Fe clusters deposited on HMS. Phase identification: (●) $\text{Co}_3\text{O}_4$ ; (▪) $\text{Fe}_2\text{O}_3$ ; (*) $\text{CoFe}_2\text{O}_4$ .	23
2.17 Proposed common reaction mechanism for the formation of diphenol in phenol hydroxylation.	24
2.18 The possible mechanisms that can occurred at various pH.	24
4.1 TGA thermogram of silatrane precursor.	37
4.2 The structure of silatrane.	38
4.3 FT-IR spectra of silatrane.	38
4.4 The SAXS patterns of SBA-15 (a) and Fe-SBA-15 containing different Fe/Si mol ratios of b) 0.01, c) 0.03, and d) 0.05.	39
4.5 The DRUV spectra of the calcined Fe-SBA-15 containing different Fe/Si mol ratios of a) 0.01, b) 0.03, and c) 0.05).	40
4.6 $\text{N}_2$ adsorption–desorption isotherms of SBA-15 a) and Fe-SBA-15 with different Fe contents of b) 0.01, c) 0.03, and d) 0.05.	41
4.7 The pore size distribution by BJH desorption of SBA-15 a) and Fe-SBA-15 with different Fe contents of b) 0.01, c) 0.03, and d) 0.05.	42
4.8 FE-SEM images of a) SBA-15, b) 0.01 Fe-SBA-15, c) 0.05 Fe-SBA-15.	44
4.9 SAXS patterns of the calcined pure SBA-15 and Ti-SBA-15 containing different amount of Ti loadings (Ti/Si mol ratio): (a) 0, (b) 0.01, and (c) 0.03.	45
4.10 The DRUV spectra of the calcined Ti-SBA-15 containing different amounts of Ti loadings: a) 0.01 and b) 0.03.	46
4.11 $\text{N}_2$ adsorption–desorption isotherms of a) SBA-15, b) 0.01 and c) 0.03 Ti-SBA-15.	47

<b>FIGURE</b>	<b>PAGE</b>
4.12 Pore size distribution by BJH desorption of a) SBA-15, b) 0.01 and c) 0.03Ti-SBA-15.	47
4.13 FE-SEM images of a) 0.01 Ti-SBA-15 and b) 0.03 Ti-SBA-15.	48
4.14 The SAXS patterns of a) SBA-15 and b) 0.01Fe-0.01Ti-SBA-15.	49
4.15 The DRUV spectrum of the calcined 0.01Fe-0.01Ti-SBA-15.	49
4.16 N <sub>2</sub> adsorption-desorption isotherms of a) SBA-15 and b) 0.01Fe-0.01Ti-SBA-15.	50
4.17 Pore size distribution by BJH desorption of a) SBA-15 and b) 0.01Ti-0.01Fe-SBA-15.	51
4.18 FE-SEM image of 0.01Fe-0.01Ti-SBA-15.	51
4.19 Effect of the reaction temperature and time on the phenol conversion using 30 mg of 0.01Fe-0.01Ti-SBA-15 and 1:1 phenol:H <sub>2</sub> O <sub>2</sub> ratio.	52
4.20 Effect of the catalyst content on the phenol conversion performed at 30 °C using 0.01Fe-0.01Ti-SBA-15 and 1:1 phenol:H <sub>2</sub> O <sub>2</sub> ratio.	53
4.21 Effect of the phenol:H <sub>2</sub> O <sub>2</sub> molar ratio performed at 30 °C using 30 mg of 0.01Fe-0.01Ti-SBA-15.	54
4.22 SAXD of the catalysts after used and calcined.	56
4.23 Common reaction mechanism for the formation of diphenol in phenol hydroxylation.	58
4.24 Phenol hydroxylation reaction pathway of Fe ions.	59
4.25 The mechanism of phenol hydroxylation to HQ via titanium.	60
4.26 The mechanism of phenol hydroxylation to CAT via titanium.	61
4.27 Schematic diagram of phenol hydroxylation with H <sub>2</sub> O <sub>2</sub> and tar formation.	61
A1 WAXD patterns of all catalysts.	72
B1 Effect of the reaction time on the selectivity of product.	76
B2 Effect of catalyst content on the selectivity of product.	76
B3 Effect of Molar ratio (Phenol/H <sub>2</sub> O <sub>2</sub> ) on the selectivity of product.	77