

**DEEP HYDROGENATION OF TETRALIN IN THE PRESENCE OF  
DIBENZOTHIOPHENE OVER Pt/Pd CATALYSTS:  
INFLUENCE OF FLUORINE**

Ms. Nitchanun Rattanapuchapong

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,  
Case Western Reserve University and Institut Français du Pétrole

2007

501988

**Thesis Title:** Deep Hydrogenation of Tetralin in the Presence of Dibenzothiophene over Pt/Pd Catalysts: Influence of Fluorine  
**By:** Nitchanun Rattanapuchapong  
**Program:** Petrochemical Technology  
**Thesis Advisors:** Dr. Siriporn Jongpatiwut  
Prof. Daniel E. Resasco  
Assoc. Prof. Thirasak Rirksomboon  
Prof. Somchai Osuwan

---

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

*Nantaya Yanumet*  
.....College Director  
(Assoc. Prof. Nantaya Yanumet)

**Thesis Committee:**

*J. hin*  
.....  
(Dr. Siriporn Jongpatiwut)

*Daniel Resasco*  
.....  
(Prof. Daniel E. Resasco)

*Thirasak Rirksomboon*  
.....  
(Assoc. Prof. Thirasak Rirksomboon)

*A. Osuwan*  
.....  
(Prof. Somchai Osuwan)

*N. Mongkolsiri*  
.....  
(Dr. Nakarin Mongkolsiri)

*Vissanu Meeyoo*  
.....  
(Assoc. Prof. Vissanu Meeyoo)

**ABSTRACT**

4871017063: Petrochemical Technology Program

Nitchanun Rattanapuchapong: Deep Hydrogenation of Tetralin in the Presence of Dibenzothiophene over Pt/Pd Catalysts: Influence of Fluorine.

Thesis Advisors: Dr. Siriporn Jongpatiwut, Prof. Daniel E. Resasco, Assoc. Prof. Thirasak Rirksomboon, and Prof. Somchai Osuwan  
47 pp.

Keywords: Deep hydrogenation/ Pt-Pd on Al<sub>2</sub>O<sub>3</sub>/ Tetralin/ Fluorine

Deep hydrogenation can greatly enhance the quality of diesel fuel by removing poly-aromatic content to meet environmental regulations. Alumina-supported Pt, Pd and Pt-Pd catalysts are well known as noble metal catalysts which are widely used in the hydrogenation reaction at low temperatures, but these catalysts are very sensitive to sulfur. Thus, the aim of this work is to develop these catalysts to enhance the S-tolerance by adding controlled amounts of fluorine both before and after metal loading. Dibenzothiophene (DBT) is used as the S-containing molecule. All of the catalysts were prepared by incipient wetness impregnation and tested at a reaction temperature of 300°C with a total pressure of 500 psig. The results showed that in the absence of sulfur, the addition of F before metal enhanced catalytic activity but the addition of F after metal reduced catalytic activity for all catalysts. The atomic surface composition obtained by XPS revealed that the oxygen concentration decreased with the addition of F because the incorporation of F replaces O or OH of the oxide catalysts. Noticeably, the concentration of residual Cl on the surface, from the metal precursors, was reduced when F was added. XPS results showed that the addition of F before the metal gave higher metal dispersion (Pd:Al ratio) than the addition of F after the metal. In the presence of DBT, the F-promoted catalysts gave a higher tetralin conversion and higher sulfur tolerance than unpromoted catalysts. For the order of impregnation, the addition of F before the metal give a higher sulfur tolerance than the addition of F after the metal.

## บทคัดย่อ

ชื่อ นามสกุล : การศึกษาผลกระทบของปรอทต่อการกัดกร่อนของหลุมผลิตก๊าซธรรมชาติในอ่าวไทย Effect of mercury on corrosion in production wells in a Gulf of Thailand fields อ. ที่ปรึกษา : รศ.ดร. จินตนา สายวรรณ ดร. คาร์เรล แอล แกลล์ป และ ดร.สุธา สุทธิเรือง วงศ์ 81 หน้า

การศึกษาการกัดกร่อนต่อวัสดุที่ใช้เป็นท่อในการผลิตก๊าซธรรมชาตินับว่ามีความสำคัญต่อการปรับลดค่าใช้จ่าย โดยในงานวิจัยนี้เลือกใช้เหล็กกล้าคาร์บอนชนิด L80 และ สเตนเลสสตีลชนิด 420 ซึ่งมีปริมาณธาตุโครเมียมเจืออยู่ 13% (โดยน้ำหนัก) เพื่อศึกษาโดยวิธีอิมเมอร์ชัน และ โพเทนทิโอสโตคานิกซ์ โพลาริเซชัน สารละลายกัดกร่อนที่นำมาใช้เป็นสารละลายจำลองของน้ำที่ผลิตได้จากหลุม โดยใช้อุณหภูมิประกอบตามข้อมูลจากหลุมผลิตจริงจากอ่าวไทย นอกเหนือจากปรอทแล้วทำการศึกษาผลกระทบของปรอทที่มีต่อสถานะต่างๆ ได้แก่ อุณหภูมิ ปริมาณความเข้มข้นคลอไรด์ ก๊าซคาร์บอนไดออกไซด์ และค่าพีเอช

พบว่าอุณหภูมิมีส่วนช่วยเร่งปฏิกิริยาในทางจลน์พลศาสตร์ ในขณะที่คลอไรด์อ็อกไซด์ (1% - 3.5% โซเดียมคลอไรด์) และก๊าซคาร์บอนไดออกไซด์เร่งการกัดกร่อนโดยการทำลายฟิล์มที่ผิวหน้าของวัสดุ โดยเฉพาะกับเหล็กกล้า 13%โครเมียม การลดค่าพีเอชทำให้ปริมาณโปรตอนในสารละลายเพิ่มมากขึ้น ซึ่งเป็นการเสริมความรุนแรงของปฏิกิริยาการรับ โปรตอนเกิดเป็นก๊าซไฮโดรเจนด้านคาโทด ในขณะที่วัสดุจะละลายออกมาในรูปของอ็อกไซด์โลหะมากขึ้น ปรอทที่ความเข้มข้นน้อยกว่า 12 ส่วนในล้านส่วน ไม่ส่งผลต่อการกัดกร่อนของวัสดุ และอุณหภูมิ (30 °C - 60°C) หรือความดันก๊าซคาร์บอนไดออกไซด์ไม่มีผลกระทบร่วมกับการกัดกร่อนของปรอท แต่หากความเข้มข้นเพิ่มมากขึ้นถึง 100 ส่วนในล้านส่วนแล้ว อัตราการกัดกร่อนจะเพิ่มขึ้นอย่างเห็นได้ชัด เนื่องจากปรอทมีค่าความต่างศักย์ขั้วไฟฟ้าสูงกว่าไฮโดรเจนอ็อกไซด์ ซึ่งนับว่าเป็นการเพิ่มปฏิกิริยาด้านคาโทดอีกหนึ่งปฏิกิริยา

## ACKNOWLEDGEMENTS

This work has been a very memorable and valuable experience as well as a lot of knowledge to the author. It would not have been succeeded without the assistance of a number of individuals including organizations. The author would like to thank all of them for making this work succeed.

I am grateful for the scholarship and funding of the thesis work provided by the Petroleum and Petrochemical College: and the National Excellence Center for Petroleum, Petrochemicals, and Advanced Materials, Thailand.

I would like to acknowledge the Thailand Research Fund, and Research Unit of Ratchadapisek Somphot Endowment, Chulalongkorn University.

I am also deeply indebted to my advisor, Dr. Siriporn Jongpatiwut, for her support, suggestion, kindness and infinite supervisions. I would like to express sincere appreciation to my co-advisors, Assoc. Prof. Thirasak Rirksomboon, Prof. Somchai Osuwan, and Prof. Daniel E. Resasco for their useful guidance, intensive suggestions, and vital helps throughout this research work. In addition, I would like to acknowledge Dr. Nakarin Mongkolsiri and Assoc. Prof. Visanu Meeyoo for serving on my thesis committee and for their comments.

Special thanks go to all PPC Ph.D. students for their friendly assistances, cheerful nesses, creative suggestions, and encouragements. Especially, Mr. Tanate Danuthai, a Ph. D. student who acted as my supervisor for this work, for his excellent suggestions and encouragements as well as making this research to be a fun filled activity. The author had the most enjoyable time working with all of them.

I also wish to give sincere thanks to all of my friends and staff of the Petroleum and Petrochemical College for giving the permission to freely use the research facilities.

I would like to extend special thanks to PPC's staff for their contributions, particularly C. P. O. Poon Arjpru for all electronic works and Mr. Sanit Prinakorn for repairing the glassware.

Finally, I would like to express deep appreciation to my parents, my sister, and my brother, who play the greatest role in my success, for their endless support and love throughout the two year study period.

## 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	viii
List of Figures	ix
 <b>CHAPTER</b>	
<b>I INTRODUCTION</b>	<b>1</b>
<b>II BACKGROUND AND LITERATURE REVIEW</b>	<b>4</b>
<b>III EXPERIMENTAL</b>	<b>17</b>
3.1 Material and Equipment	17
3.1.1 Chemicals	17
3.1.2 Gas	17
3.1.3 Equipment	18
3.2 Catalyst Preparation	18
3.3 Catalyst Characterization	19
3.3.1 Temperature Programmed Reduction	19
3.3.2 H <sub>2</sub> Pulse Chemisorption	20
3.3.3 X-ray Photoelectron Spectroscopy	20
3.3.4 Atomic Adsorption Spectroscopy	21
3.4 Catalytic Activity Testing	21

<b>CHAPTER</b>	<b>PAGE</b>
<b>IV RESULTS AND DISCUSSION</b>	25
4.1 Catalyst Preparation	25
4.2 Catalyst Characterization	25
4.2.1 Temperature Programmed Reduction	25
4.2.2 H <sub>2</sub> Pulse Chemisorption	29
4.2.3 X-ray Photoelectron Spectroscopy	30
4.2.4 Atomic Adsorption Spectroscopy	31
4.3 Catalytic Activity Testing	32
4.3.1 Hydrogenation of Tetralin	32
4.3.2 Inhibition of Hydrogenation Activity by Sulfur Compounds	39
<b>V CONCLUSIONS AND RECOMMENDATIONS</b>	42
<b>REFERENCES</b>	43
<b>CURRICULUM VITAE</b>	47

## LIST OF TABLES

TABLE		PAGE
2.1	Cetane number and auto-ignition temperature of hydrocarbons	5
2.2	Aromatic compounds in Kuwait Atmospheric Gas Oil	7
2.3	Typical structures of some aromatic compounds present in petroleum fraction	8
2.4	Current and proposed sulfur levels in diesel in Asia, EU and USA	12
4.1	List of the dispersion degree (%) of Pt, Pd, and PtPd catalyst with and without F-promoter which calcined at 500°C	30
4.2	Atomic surface composition (mol%) of different catalysts which calcined at 500°C obtained by XPS analysis	31
4.3	Chemical composition of the catalysts determined by AAS	31
4.4	List of conversions of Pt, Pd, and PtPd with and without F-promoter	36



## LIST OF FIGURES

FIGURE	PAGE
1.1 Sequential hydrogenation reaction of naphthalene.	2
2.1 Structure of related polycyclic sulfur compounds found in diesel fuels.	9
3.1 Schematic flow diagram of temperature programmed reduction.	20
3.2 Schematic flow diagram of hydrogenation reaction.	23
3.3 Experimental apparatus of hydrogenation reaction.	24
4.1 TPR profiles of Pt/Al <sub>2</sub> O <sub>3</sub> , PtF/Al <sub>2</sub> O <sub>3</sub> and FPt/Al <sub>2</sub> O <sub>3</sub> catalyst.	27
4.2 TPR profiles of Pd/Al <sub>2</sub> O <sub>3</sub> , PdF/Al <sub>2</sub> O <sub>3</sub> and FPd/Al <sub>2</sub> O <sub>3</sub> catalyst.	28
4.3 TPR profiles of PtPd/Al <sub>2</sub> O <sub>3</sub> , PtPdF/Al <sub>2</sub> O <sub>3</sub> and FPtPd/Al <sub>2</sub> O <sub>3</sub> catalyst.	29
4.4 The overview of metal dispersion and conversion among catalysts.	34
4.5 Effect of sulfur in the feed stock and F-promoted support on the tetralin hydrogenation selectivity for different catalysts.	35
4.6 Conversion of tetralin as a function of time on stream (TOS) over Pt catalyst. Reaction condition: 500 psig, 300°C, H <sub>2</sub> /HC=11.	37
4.7 Conversion of tetralin as a function of time on stream (TOS) over Pd catalyst. Reaction condition: 500 psig, 300°C, H <sub>2</sub> /HC=11.	37
4.8 Conversion of tetralin as a function of time on stream (TOS) over PtPd catalyst. Reaction condition: 500 psig, 300°C, H <sub>2</sub> /HC=11.	38

FIGURE	PAGE
4.9 Conversion of tetralin as a function of time on stream (TOS) over Pt, Pd and PtPd catalyst. Reaction condition: 500 psig, 300°C, H <sub>2</sub> /HC=11.	38
4.10 Conversion of tetralin in the presence of DBT as a function of time on stream (TOS) over Pt, Pd and PtPd catalyst. Reaction condition: 500 psig, 300°C, H <sub>2</sub> /HC=11.	39
4.11 Conversion of tetralin in the presence of DBT as a function of time on stream (TOS) over Pt catalyst. Reaction condition: 500 psig, 300°C, H <sub>2</sub> /HC=11.	40
4.12 Conversion of tetralin in the presence of DBT as a function of time on stream (TOS) over Pd catalyst. Reaction condition: 500 psig, 300°C, H <sub>2</sub> /HC=11.	41
4.13 Conversion of tetralin in the presence of DBT as a function of time on stream (TOS) over PtPd catalyst. Reaction condition: 500 psig, 300°C, H <sub>2</sub> /HC=11.	41