PT/HY^{core}-PD/TIO₂^{shell} CATALYSTS FOR THE ONE-POT REACTION OF JATROPHA OIL TO BIOJET FUEL

Vorachit Umnuayporn

A Thesis Submitted in Partial Fulfillment 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

2015

I 28368824

580061

0

Thesis Title:	Pt/HY ^{core} -Pd/TiO ₂ ^{shell} Catalysts for the One-pot Reaction of
	Jatropha Oil to Biojet Fuel
By:	Vorachit Umnuayporn
Program:	Petroleum Technology
Thesis Advisor:	Assoc. Prof. Siriporn Jongpatiwut

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

College Dean

(Asst. Prof. Pomthong Malakul)

Thesis Committee:

0

.....

(Assoc. Prof. Siriporn Jongpatiwut)

0 Aleman

(Assoc. Prof. Thirasak Rirksomboon)

T. Dun than

(Dr. Tanate Danuthai)

ABSTRACT

5673033063:

Vorachit Umnuayporn: Pt/HY^{core}-Pd/TiO₂^{shell} Catalysts for the One-

pot Reaction of Jatropha Oil to Biojet Fuel.

Petroleum Technology Program

Thesis Advisor: Assoc. Prof. Siriporn Jongpatiwut 67 pp.

Keywords:

Deoxygenation/ Hydrocracking/ Hydroisomerization/ Hydrotreated Renewable Jet Fuel/ Jatropha Oil

Biojet fuel is obtained by the hydrodeoxygenation of triglycerides followed by hydrocracking and hydroisomerization reactions of the intermediate long chain hydrocarbons. In our previous studies, the catalysts for the two reactions were Pd/TiO₂ and Pt/HY respectively. In this research, the two catalysts were combined into Pt/HY^{core}-Pd/TiO₂^{shell} catalysts with different Pd/TiO₂^{shell} compositions (i.e. 31 %, 36 %, 44 %, and 57 wt%). The catalytic activities of the core-shell catalyst were tested in a continuous flow fixed bed reactor, compared with the pure Pt/HY, Pd/TiO₂ and physical mixture of the two catalysts. XRD, TEM, BET, TPD, TPR, and AAS results showed that Pt/HY^{core}-Pd/TiO2^{shell} catalysts were successfully synthesized without losing Pt/HY and Pd/TiO₂ catalyst properties. The core-shell catalysts with Pd/TiO2^{shell} of 31 %, 36 %, 44 %, and 57 % exhibited 100 % conversion of triglycerides into gasoline, jet, and diesel fuel range products while Pt/HY catalyst exhibited very low conversion of triglycerides with high oxygenate products and Pd/TiO₂ catalyst only converted to diesel range paraffin hydrocarbons. The products obtained over core-shell catalyst were shorter chain hydrocarbons compared to those obtained from the physical mixing catalyst due to its core-shell mechanism that jatropha oil was first deoxygenated in Pd/TiO2^{shell} before further cracked in Pt/HY^{core}. Among all prepared catalysts, the core-shell catalyst with 36 % Pd/TiO_2^{shell} gave the highest biojet fuel yield of 40 % at TOS of 2 h.

บทคัดย่อ

วรชิต อำนวยพร : การผลิตน้ำมันเจ็ทจากน้ำมันสบู่ดำโดยใช้ตัวเร่งปฏิกิริยา Pt/HY^{core}-Pd/TiO₂^{shell} (Pt/HY^{core}-Pd/TiO₂^{shell} Catalysts for the One-pot Reaction of Jatropha Oil to Biojet Fuel) อ. ที่ปรึกษา : รศ. ดร. ศิริพร จงผาติวุฒิ 67 หน้า

การผลิตน้ำมันเจ็ทที่มาจากพลังงานหมุนเวียน เริ่มจากน้ำมันที่มีส่วนผสมของไตรกลีเซอ ไรด์ผ่านปฏิกิริยาไฮโดรดิออกซิจิเนชันตามด้วยปฏิกิริยาไฮโดรแครกกิง และ ปฏิกิริยาไฮโดรไอโซ เมอไรเซชันของสารมัธยันตร์ที่เป็นไฮโครคาร์บอนสายยาว การศึกษาที่ผ่านมาได้ใช้ตัวเร่งปฏิกิริยา Pd/TiO, และ Pt/HY ตามลำคับ งานวิจัยนี้ได้นำตัวเร่งปฏิกิริยาทั้งสองตัวมารวมเป็นตัวเร่งปฏิกิริยา คอร์เซลล์ในสัคส่วนต่างๆ ตัวเร่งปฏิกิริยาคอร์เซลล์ที่เตรียมขึ้นจะถูกนำมาทคสอบความว่องไวใน การเร่งปฏิกิริยาจากน้ำมันสบู่คำเป็นน้ำมันเจ็ท โดยใช้เครื่องปฏิกรณ์แบบเบคนิ่งชนิดไหลต่อเนื่อง ผลการวิเคราะห์ตัวเร่งปฏิกิริยาโดยใช้เทคนิค XRD, TEM, BET, TPD, TPR และ AAS แสดงให้ เห็นว่าตัวเร่งปฏิกิริยาคอร์เซลล์ที่เตรียมขึ้นยังคงคุณสมบัติของตัวเร่งปฏิกิริยา Pt/HY และ Pd/TiO, ไว้ ตัวเร่งปฏิกิริยาคอร์เชลล์ที่สัคส่วนน้ำหนัก Pd/TiO, ที่ 31 %, 36 %, 44 % และ 57 % สามารถ แปรงสภาพน้ำมันสบู่ดำทั้งหมดเป็นไฮโครคาร์บอนในช่วงจุดเดือดของน้ำมันแกโซลีน น้ำมันเจ็ท และ น้ำมันดีเซล ในขณะที่ตัวเร่งปฏิกิริยา Pt/HY แปรงสภาพน้ำมันสบู่ดำได้ต่ำและได้ผลิตผลของ ้ออกซิจิเนตเป็นหลัก และตัวเร่งปฏิกิริยา Pd/TiO, ได้ผลิตผลไฮโดรคาร์บอนโซ่ตรงในช่วงน้ำมัน ้ดีเซล ผลผลิตไฮโดรคาร์บอนจากตัวเร่งปฏิกิริยาคอร์เชลล์โซ่สั้นกว่าเมื่อเทียบกับผลผลิตจากตัวเร่ง ้ปฏิกิริยาที่ผสมทางกายภาพในสัดส่วนเดียวกันเพราะกลไกของคอร์เชลล์ เนื่องจากไตรกลีเซอไรด์ ้ผ่านปฏิกิริยาไฮโครคีออกซิจิเนชันในตัวเร่งปฏิกิริยา Pd/TiO, ก่อนที่จะผ่านปฏิกิริยาไฮโครแครก กิ่งในตัวเร่งปฏิกิริยา Pt/HY ในจำนวนตัวเร่งปฏิกิริยาที่ได้เตรียม ตัวเร่งปฏิกิริยาคอร์เชลล์ที่สัดส่วน Pd/TiO, 36 % ได้ผลผลิตน้ำมันเจ็ทได้สูงสุดที่ 40 %

ACKNOWLEDGEMENTS

For the success of this thesis, I would like to thank many people and organization who have contributed to my thesis work.

First of all, I would like to take this chance to sincerely thank my advisor, Assoc. Prof. Siriporn Jongpatiwut, for her helpful suggestions, discussions, and supervision from the very early stage of this research.

I would like to thank Dr. Suchada Butnark and Mr. Chaiwat Tachakritikul for suggestion and discussion throughout this research work.

I would like to thank Assoc. Prof. Thirasak Rirksomboon and Dr. Tanate Danuthai for kindly serving on my thesis committee. Their suggestions are certainly important and helpful for completion of this thesis.

I would like to thank all faculty and staff at the Petroleum and Petrochemical College, Chulalongkorn University for their kind assistance and cooperation.

This research work was partially supported by the Ratchadapisek Sompoch Endowment Fund (2013), Chulalongkorn University (CU-56-900-FC), Thailand Research Fund (IRG5780012), Center of Excellence on Petrochemical and Materials Technology, and PTT Public Company Limited, Thailand.

I would like to thank Ms. Tepin Hengsawad, Mr. Sikarin Tamiyakul and all of my friends at PPC for friendly support, encouragement, cheerfulness, and assistance. Without them, two years in PPC would have been meaningless for me. I had the most enjoyable time working with all of them.

Finally, I would like to express my sincere gratitude to thank my family, for showing me the joy of intellectual pursuit ever since I was a child, for standing by me and for understanding every single part of my mind.

TABLE OF CONTENTS

o

Title Page	i	
Abstract (in English)	iii	4
Abstract (in Thai)	iv	
Acknowledgements	v	
Table of Contents	vi	
List of Tables	ix	
List of Figures	x	

CHAPTER

Ι	INTRODUCTION	1
II	LITERATURE REVIEW	3
	2.1 Renewable Diesel	3
	2.2 Hydrotreated Renewable Jet Fuel	7
	2.3 Raw Materials in Hydrotreated Renewable Jet	
	Production	8
	2.4 Core-shell Catalyst	9
	2.4.1 Effect of the Pd NPs Location in the Core-Shell	
	Catalyst	10
	2.4.2 Effect of Pore Diameter in the Ti-MS Shell	14
	2.4.3 Effect of the Ti-MS Shell Thickness	17
III	EXPERIMENTAL	23
	3.1 Materials	23
	3.1.1 Feedstock	23
	3.1.2 Chemicals	23
	3.1.3 Gases	23

σ

CHA	PT	ER
-----	----	----

IV

PAGE

3.2	Equip	oment	24
	3.2.1	Preparation and Characterization of Core-shell	
		Catalyst	24
	3.2.2	Catalyst Performance Testing	24
3.3	Metho	odology	25
	3.3.1	Catalyst Preparation	25
	3.3.2	Catalyst Characterization	26
	3.3.3	Catalytic Activity Testing	29
	3.3.4	Product Analysis	31
RE	SULT	S AND DISCUSSION	34
4.1	Chara	acterization of Fresh Catalysts	34
	4.1.1	Iransmission Electron Microscopy (TEM)	34
	4.1.2	X-ray Diffraction (XRD)	39
	4.1.3	Brunauer-Emmett-Tellet (BET)	40
	4.1.4	Atomic Absorption Spectroscopy (AAS)	41
	4.1.5	Temperature Programmed Reduction (TPR)	42
	4.1.6	Temperature Programmed Desorption (TPD)	
		of Isopropylamine	43
4.2	Feed	and Standard Analysis	45
	4.2.1	Standard Analysis	45
	4.2.2	Feed Analysis	47
4.3	Catal	ytic Activity Testing	49
	4.3.1	Effect of LHSVs	49
	4.3.2	Effect of Pd/TiO ₂ Composition	50
	4.3.3	Effect of Core-shell Catalysts	53
	4.3.4	Effect of Feeds	54
4.4	Chara	acterization of Spent Catalysts	55
	4.4.1	Temperature Programmed Oxidation (TPO)	55
	4.4.2	X-ray Diffraction of Spent Catalyst (XRD)	57

σ

.

CHAPTER	2	PAGE	
V	CONCLUSIONS AND RECOMMENDATIONS	58	
	5.1 Conclusions	58	
	5.2 Recommendations	58	
	REFERENCES	59	
	APPENDIX	61	
	Appendix A Standard Analysis	61	
	CURRICULUM VITAE	67	

•

ο

LIST OF TABLES

TABL	BLE	
2.1	Summary of catalyst sample parameters, activity, and	
	selectivity for one-pot oxidation	20
2.2	Conversion and yield of bioliquid fuel in the catalytic	
	conversion of jatropha oil	21
3.1	Description of flow diagram of the hydrocracking of n-	
	paraffin feedstocks experiment in high pressure packed-bed	÷
	continuous flow reactor system	31
3.2	The reaction conditions for one-pot reaction of jatropha oil.	31
3.3	The chromatographic temperature program for liquid	
	product analysis	32
3.4	The chromatographic temperature program for gas-phase	
	product analysis	33
4.1	Physical characteristics of the prepared Pt/HY, S31, S36,	
	S44, S57, and Pd/TiO ₂ catalysts	41
4.2	Acidity of the prepared catalysts from TPD of	
	isopropylamine	44
4.3	Composition of jatropha oil	48
4.4	Fatty acid composition of jatropha oil	48
4.5	Liquid and gas products yield at operating condition: 310	
	°C, 500 psig, LHSV of 0.5 h^{-1} , H ₂ /feed molar ratio of 60,	
	and TOS of 2 h	51
4.6	Amount of carbon deposits on prepared catalyst after	
	reaction	55

0

-

LIST OF FIGURES

۰

FIGURE		PAGE
2.1	Flowchart for transformation of lipid materials (biodiesel	
	and renewable diesel by hydrodeoxygenation) to products	
	of engine combustion.	4
2.2	The reaction pathway for conversion of triglycerides to	
	renewable diesel.	5
2.3	The possible liquid-phase reaction pathways for	
	production of straight- chain hydrocarbons from fatty	
	acids.	6
2.4	Gas phase reactions of CO or CO_2 with H_2 or H_2O_2 .	6
2.5	Schematic illustration of the one-pot oxidation reaction	
	using (a) Pd/TS-1 and (b) the Pd/SiO ₂ @Ti-MS core-shell	
	catalyst.	10
2.6	HR-TEM images and schematic illustrations (insets) of	
	(a,b) $Pd/SiO_2@Ti-MS$, (c,d) $SiO_2/@Pd(R)/Ti-MS$, and	
	(e,f) $SiO_2/@Pd(S)/TiMS$.	12
2.7	(A) Ti-MS shell parameters and metal contents of	
	samples. (B) Amount of H_2O_2 synthesized using	
	$Pd/SiO_2@Ti-MS$, $SiO_2/@Pd(R)/Ti-MS$, and	
	$SiO_2/@Pd(S)/Ti-MS.$ (C) (a) Kinetics of methylphenyl	
	sulfide (1) oxidation using in situ generated H_2O_2 , and (b)	
	dependence of the conversion level on the selectivity.	
	Selectivity = $[2/(2+3)] \times 100$. (D) Catalytic activity and	
	selectivity for sulfoxide in the one-pot oxidation of methyl	
	phenyl sulfide and diphenyl sulphide.	13

.

PAGE

FIGURE

- 2.8 (A) (a) N₂ adsorption-desorption isotherms and (b) BJH pore size distributions. (B) TEM images of Pd/SiO₂@Ti-MS type core-shell catalysts using (a) C₁₂TABr, (b) C₁₄TABr, (c) C₁₆TABr, and (d) C₁₈TACl as template SDAs. (C) Parameters of the Ti-MS shells.
- 2.9 (a,c) Kinetics of methyl phenyl sulfide (1) and diphenyl sulfide (4) oxidation using in situ generated H₂O₂, and (b,d) dependence of the conversion level on the selectivity using Pd/SiO₂@Ti-MS type core-shell catalysts with controlled pore diameters.
- 2.10 TEM images of Pd/SiO₂@Ti-MS type core-shell catalysts with various shell thicknesses, prepared by changing the amount of precursor: (a) 1×, (b) 3×, (c) 5×, and (d) 7×. (e) Ti-MS shell parameters and metal contents of the catalyst samples.
- 2.11 (a) Kinetics of methyl phenyl sulfide one-pot oxidation and (b) dependence of the conversion level on the selectivity using Pd/SiO₂@Ti-MS or SiO₂@Pd(S)/Ti-MS type core-shell catalysts with various shell thicknesses (different amounts of precursors; 1, 3, 5, and 7 times the original amount).
- 2.12 Possible cracking mechanism of triglyceride over composite catalyst. A- propane or propene, B- CO or CO₂, C- long chain hydrocarbons, X- C1–C3 hydrocarbons, Y both straight chain and branched hydrocarbons (C_nH_{2n+2}) and aromatics.

18

16

19

0

3.1	Schematic of the reactor system.	30
4.1	(a), (b) TEM images and (c) EDX spectrum of Pt/HY	
	catalyst.	35
4.2	(a), (b), (c) TEM images and (d) EDX spectrum of	
	Pd/TiO ₂ catalyst.	36
4.3	(a), (b) TEM images of S31 catalyst and (c), (d) EDX	
	spectra of Pd/TiO_2 catalyst.	37
4.4	(a), (b) TEM images of S36 catalyst.	38
4.5	(a), (b) TEM images of S44 catalyst.	38
4.6	(a), (b) TEM images of S57 catalyst.	39
4.7	XRD patterns of synthesized Pt/HY, S31, S36, S44, S57,	
	and Pd/TiO_2 catalysts, (dashed line: anatase).	40
4.8	Pore size distributions of the prepared Pt/HY, S31, S36,	
	S44, S57, and Pd/TiO ₂ catalysts.	41
4.9	Temperature programmed reduction (TPR) profiles of the	
	prepared Pt/HY, S31, S36, S44, S57, and Pd/TiO $_2$	
	catalysts.	43
4.10	TPD profiles of prepared Pt/HY, S31, S36, S44, S57, and	
	Pd/TiO ₂ catalysts.	44
4.11	Chromatograms of standard <i>n</i> -alkanes.	45
4.12	(a) Liquid products, (b) liquid products chromatogram,	
	and (c) gas products chromatogram over S44 catalyst	
	operated at operating conditions: 310 °C, 500 psig, LHSV $^-$	
	of 0.5 h^{-1} , H ₂ /feed molar ratio of 60, and TOS of 4 h.	46
4.13	Chromatogram of jatropha oil.	48
4.14	Products yield from one-pot reaction of jatropha oil over	
	S36 and S44 catalyst at operating condition: 310 °C, 500	
	psig, H_2 /feed molar ratio of 60, and TOS of 2 h.	49

σ

0

-

.

ο

•

PAGE

4.15	Products yield from one-pot reaction of jatropha oil over	
	Pt/HY, S31, S36, S44, S57 and Pd/TiO $_2$ catalyst at	
	operating condition: 310 °C, 500 psig, LHSV of 0.5 h ⁻¹ ,	
	H_2 /feed molar ratio of 60, and TOS of 2 h.	50
4.16	Liquid gasoline yield from one-pot reaction of jatropha	
	oil over Pt/HY ^{core} -Pd/TiO ₂ ^{shell} catalyst at operating	
	condition: 310 °C, 500 psig, LHSV of 0.5 h^{-1} , H ₂ /feed	
	molar ratio of 60.	52
4.17	Liquid jet yield from one-pot reaction of jatropha oil over	
	Pt/HY ^{core} -Pd/TiO ₂ ^{shell} catalyst at operating condition: 310	
	°C, 500 psig, LHSV of 0.5 h^{-1} , H ₂ /feed molar ratio of 60.	
	Liquid diesel yield from one-pot reaction of jatropha oil	52
4.18	over Pt/HY ^{core} -Pd/TiO ₂ ^{shell} catalyst at operating condition:	
	310 °C, 500 psig, LHSV of 0.5 h^{-1} , H ₂ /feed molar ratio of	
	60.	53
4.19	Liquid products yield from one-pot reaction of jatropha	
	oil over Pt/HY, S36, S36p, and Pd/TiO ₂ catalysts at	
	operating condition: 310 °C, 500 psig, LHSV of 0.5 h ⁻¹ ,	
	H_2 /feed molar ratio of 60, and TOS of 2 h.	54
4.20	Product yields from one-pot reaction of diesel fuel over	
	S36 catalyst at operating condition: 310 °C, 500 psig,	
	LHSV of 0.5 h ⁻¹ , H_2 /feed molar ratio of 60.	55
4.21	TPO profiles of physical mixing, Pt/HY, S31, S36, S44,	
	and Pd/TiO_2 catalysts after 8 h course of reaction.	56
4.22	XRD patterns of Pt/HY, S36, Spent S36 and Pd/TiO $_2$	
	catalysts, (dashed line: anatase).	57

÷