

**CATALYTIC PYROLYSIS OF WASTE TIRE USING NICKEL PROMOTED
CATALYSTS AND CORE-SHELL COMPOSITES**

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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

I28368988

Thesis Title: Catalytic Pyrolysis of Waste Tire Using Nickel Promoted Catalysts and Core-shell Composites
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Program: Petrochemical Technology
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Accepted by The Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfillment of the requirements for the Degree of Master of Science.



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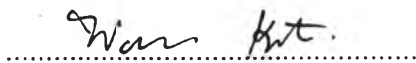
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ABSTRACT

5671034063: Petrochemical Technology Program

Witsarut Namchot: Catalytic Pyrolysis of Waste Tire Using Nickel Promoted Catalysts and Core-Shell Composites

Thesis Advisor: Assoc. Prof. Sirirat Jitkarnka 164 pp.

Keywords: Tire/ Pyrolysis/ HBETA/ HY/ HMOR/ KL/ HZSM-5/ Nickel/ MCM-41/ Core-shell/ Composite/ Sulfur

In this work, the effects of nickel-promoted catalysts and different zeolite cores of core-shell structure composite materials on the species of waste tire pyrolysis products are investigated. Ni-doped catalysts were expected to enhance of the formation of petrochemical and reduce of sulfur content in tire-derived oil. In addition, HY/MCM-41 and HBETA/MCM-41 core-shell composite were expected to reduce the formation of polycyclic aromatics and enhance the petrochemical in tire-derived oil. Furthermore, the different zeolite cores were expected to give different petrochemical selectivity. From the experimental results, nickel on different zeolite supports enhance the reduction of sulfur content in oil and promote aromatic formation, but the selectivity of hydrocarbons products and desulfurization activity depended on the zeolite supports. In order to obtain the oil with the high petrochemicals and low sulfur contents by using Ni promoter, the zeolite supports must have a suitable pore size (5.5-7 Å) and 1D channel structure that allows hydrocarbons and sulfur compounds can stay inside the pore at enough contact time for forming of valuable petrochemical and sulfur removal of sulfur compounds. For the second scope of work, The HBETA/MCM-41 and HY/MCM-41 core-shell composite were successfully synthesized, the MCM-41 shell thickness of both composite were varied in the range of 50-100 nm. The both core-shell composite catalysts provide a higher cracking and sulfur removing activities and better petrochemical selectivity than the non-composite catalysts. Different zeolite cores were found to govern different petrochemical species, HY core selectively produced ethylbenzene and toluene, whereas HBETA core selectively produced benzene, ethylbenzene and toluene.

บทคัดย่อ

วิศรุตม์ นามโชติ:ไพโรไลซิสของยางรถยนต์หมดสภาพโดยใช้ตัวเร่งปฏิกิริยาที่ปรับปรุงด้วยนิกเกิล และคอมพอสิตที่มีโครงสร้างแบบ Core-shell (Catalytic Pyrolysis of Waste Tire Using Ni- Promoted Catalysts and Core-shell Composites) อ. ที่ปรึกษา: รศ. ดร. ศิริรัตน์ จิตการคำ 164 หน้า

งานวิจัยนี้ศึกษาผลของการเติมโลหะนิกเกิลบนตัวรองรับต่างชนิดกันและผลของการใช้ซีโอไลต์ที่ต่างชนิดกันใน core ของตัวเร่งปฏิกิริยาคอมพอสิตที่มีโครงสร้างแบบ core-shell ต่อผลิตภัณฑ์ที่ได้จากการไพโรไลซิส การเติมโลหะนิกเกิลบนตัวรองรับต่างๆอาจจะทำให้เพิ่มสารแอโรแมติกในเชิงปิโตรเคมีและลดปริมาณกำมะถันในน้ำมัน นอกจากนี้การใช้ตัวเร่งปฏิกิริยาคอมพอสิตที่มีโครงสร้างแบบ core-shell ที่ประกอบขึ้นจาก HY/MCM-41 และ ตัวเร่งปฏิกิริยาคอมพอสิตที่มีโครงสร้างแบบ core-shell ที่ประกอบขึ้นจาก HBETA และ MCM-41 อาจจะสามารถลดสารแอโรแมติกขนาดใหญ่ และเพิ่มสารแอโรแมติกในเชิงปิโตรเคมีในน้ำมัน นอกจากนี้ได้การใช้ซีโอไลต์ต่างชนิดกันใน core ของตัวเร่งปฏิกิริยาคอมพอสิตที่มีโครงสร้างแบบ core-shell อาจจะทำให้ความจำเพาะเจาะจงต่อการผลิตสารแอโรแมติกในเชิงปิโตรเคมีที่แตกต่างกัน จากผลการทดลองพบว่า การเติมโลหะนิกเกิลบนซีโอไลต์ต่างชนิดกัน สามารถลดปริมาณสารกำมะถันในน้ำมันและช่วยเพิ่มสารแอโรแมติก แต่ความจำเพาะเจาะจงต่อการผลิตสารไฮโดรคาร์บอนและความสามารถในการกำจัดกำมะถันจะแตกต่างกันขึ้นอยู่กับชนิดตัวรองรับซีโอไลต์ การปรับปรุงตัวเร่งปฏิกิริยาด้วยโลหะนิกเกิล จะต้องเลือกใช้ตัวรองรับซีโอไลต์ที่มีขนาดรูเปิดที่เหมาะสม ระหว่าง 5.5 ถึง 7 อังสตรอม และมีโครงสร้างไม่ซับซ้อน (หนึ่งมิติ) ซึ่งเพียงพอที่จะทำให้สารประกอบไฮโดรคาร์บอนและสารประกอบกำมะถัน สามารถอยู่ในรูเปิดได้ในระยะเวลาที่เหมาะสมให้กลายเป็นสารแอโรแมติกที่มีความสำคัญในเชิงปิโตรเคมีและกำจัดกำมะถันในสารประกอบกำมะถัน เพื่อที่จะได้น้ำมันที่มีองค์ประกอบของสารแอโรแมติกที่มีความสำคัญในเชิงปิโตรเคมีสูงและมีปริมาณกำมะถันน้อย สำหรับงานวิจัยอีกส่วนนั้น ตัวเร่งปฏิกิริยาคอมพอสิตที่มีโครงสร้างแบบ core-shell ทั้งสองตัว ได้แก่ HY/MCM-41 และ HBETA/MCM-41 ถูกสังเคราะห์ขึ้นได้สำเร็จ โดยความหนาของ shell ของทั้งสองคอมพอสิตจะไม่สม่ำเสมอ ซึ่งจะอยู่ระหว่าง 50 ถึง 100 นาโนเมตร ตัวเร่งปฏิกิริยาคอมพอสิตที่มีโครงสร้างแบบ core-shell ทั้งสองตัวนั้น เพิ่มการแตกพันธะของสารโมเลกุลใหญ่ให้เป็นสารโมเลกุลเล็กลง (Cracking) และช่วยปรับปรุงความสามารถในการกำจัดกำมะถันและเพิ่มความจำเพาะเจาะจงใน

การผลิตสารแอรโม่ติกในเชิงปิโตรเคมีได้ดีกว่าการใช้ตัวเร่งปฏิกิริยาแบบไม่ใช้การคอมพอสิต การใช้ซีโอไลต์ต่างชนิดกันเป็นองค์ประกอบ core ของตัวเร่งปฏิกิริยาคอมพอสิต พบว่าจะควบคุมการผลิตสารแอรโม่ติกต่างชนิดกัน การใช้ core ที่เป็น HY จะมีความจำเพาะเจาะจงต่อการผลิตเอทิลเบนซีนและโทลูอิน ในขณะที่การใช้ core ที่เป็น HBETA นั้นจะมีความจำเพาะเจาะจงต่อการผลิตเบนซีน เอทิลเบนซีน และโทลูอิน

ACKNOWLEDGEMENTS

This work was accomplished with the assistance, facilities and generous assistance from all nice following people and organization as follows;

First of all, I would like to take this opportunity to give a special acknowledgement to my advisor, Assoc. Prof. Sirirat Jitkarnka, who is the most responsible for helping me complete the work, intensive attention, valuable recommendation, important supports, and encouragement throughout this work.

Unforgettably, I am grateful for valuable guidance and comments by my thesis committee, Assoc. Prof. Apanee Luengnaruemitchai and Asst. Prof. Bussarin Ksapabutr.

I would like to thank for the scholarship and the mutual financial supports of this thesis work by The Petroleum and Petrochemical College, the Center of Excellence on Petrochemical and Materials Technology, and Thailand Research Fund.

This research work was partially supported by the Ratchadapisek Sompoch Endowment Fund (2013), Chulalongkorn University (CU-56-900-FC) and Thailand Research Fund (IRG5780012).

My gratitude is extended to all staff of The Petroleum and Petrochemical College for kind helps, valuable suggestions and other important supports throughout my study period at PPC.

Moreover, I would like to give appreciation to all my friends who shared their friend cheerful, valuable suggestions and useful assistance.

In addition. I am deeply grateful to my family for their love, encouragement, understanding and all supports.

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ABBREVIATIONS

1D	One-dimension
3D	Three-dimension
ASTM	American Society for Testing and Materials
BT	Benzothiophenes
BTX	Benzene, Toluene, and Xylenes
BTz	Benzothiazoles
DBT	Dibenzothiophenes
di	Di-aromatics
E	Ethylbenzene
FID	Flame ionization detector
GC	Gas chromatography
HVGO	Heavy vacuum gas oil
ID	Internal diameter
ITC	Isothiocyanates
IWI	Incipient wetness impregnation
LVGO	Light vacuum gas oil
mono	Mono-aromatics
MS	Mass spectrometry
nap	Naphthenes
NT	Naphthothiophenes
ole	Olefins
para	Paraffins
polar	Polar-aromatics
poly	Poly-aromatics
SIMDIST	Simulated distillation
TCD	Thermal conductivity detector
TG/DTA	Thermogravimetric/Differential Thermal Analysis
Th	Thiophenes
TOF	Time of Flight

TPDRO	Temperature-programmed desorption/reduction/oxidation
TPR	Temperature-programmed reduction
XPS	X-Ray photoelectron spectroscopy
XRD	X-Ray diffraction