

**CATALYTIC TAR REMOVAL BY Ni SUPPORTED ON
CeO₂-ZrO₂ BASED CATALYSTS**

Asawin Bampenrat


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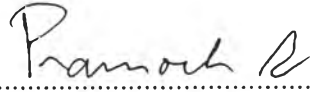
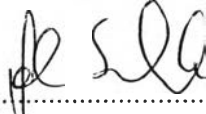
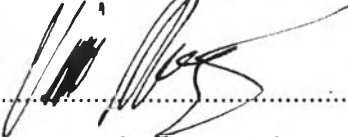

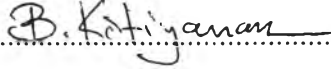
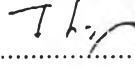

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By: Asawin Bampenrat
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Thesis Advisors: Assoc. Prof. Pramoch Rungsunvigit
Prof. Johannes W. Schwank
Assoc. Prof. Vissanu Meeyoo
Assoc. Prof. Thirasak Rirksomboon
Asst. Prof. Boonyarach Kitiyanan

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


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

Thesis Committee:

 (Prof. Somchai Osuwan)	 (Assoc. Prof. Pramoch Rungsunvigit)
 (Prof. Johannes W. Schwank)	 (Assoc. Prof. Vissanu Meeyoo)
 (Assoc. Prof. Thirasak Rirksomboon)	 (Asst. Prof. Boonyarach Kitiyanan)
 (Asst. Prof. Siriporn Jongpatiwut)	 (Assoc. Prof. Metta Charoenpanich)

ABSTRACT

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Biomass gasification is a promising technology for producing CO- and H₂-rich gases to be used for many applications. However, the presence of heavy organic impurities in the flue gas, i.e. tar, is the main technical barrier in the biomass gasification process, making catalytic hot gas conditioning a necessary step in most gasification application. Therefore, there has been emphasis on the development of highly active and carbon formation resistance catalyst for tar elimination. In this study, the total oxidation and steam reforming of model tar compounds (benzene, toluene and naphthalene) over CeO₂-ZrO₂ and Ni/CeO₂-ZrO₂-based catalysts were investigated. The experimental results showed that Mn-doped CeO₂-ZrO₂ mixed oxides, Ce_{0.75}Zr_{0.15}Mn_{0.10}O₂ particularly, catalyst exhibits the highest activity toward complete oxidation of the three studied tar compounds. Based on kinetic study results of naphthalene oxidation over CeO₂-ZrO₂ mixed oxides, the reaction mechanism can be expressed by the Mars-van Krevelen mechanism, indicating that the catalytic activity was related to the redox properties of the catalysts. For steam reforming reaction, Ni/Ce_{0.75}Zr_{0.25-x}Mn_xO₂ and Ni/Ce_{0.75}Zr_{0.15}Me_{0.10}O₂ (Me = Cr, Fe, Mn and V) catalysts exhibit high activities and stabilities for toluene and naphthalene steam reforming with no sign of deactivation in a period of 6 hours. In particular, the incorporation of Mn into ceria-zirconia mixed oxide is able to modify the redox

properties of the mixed oxide support. Moreover, the presence of Mn results in the dramatic decrease in carbon formation with the absence of filamentous carbon.

บทคัดย่อ

อศวิน บำเพ็ญรัตน์ : การกำจัดสารประกอบทาร์โดยใช้ตัวเร่งปฏิกิริยานิกเกิลบนตัวรองรับชนิดซีเรีย-เซอร์โคเนีย (Catalytic Tar Removal by Ni Supported on CeO₂-ZrO₂ Based Catalysts) อ. ที่ปรึกษา : รศ.ดร. ปราโมช รังสรรค์วิจิตร ศ. โจอานเนส ชวางค์รศ. ดร. วิษณุ มีอยู่ รศ. ดร. ชีรศักดิ์ ฤกษ์สมบูรณ์ และ ผศ. ดร. บุญรัชต์ กิตติยานันท์ 124 หน้า

กระบวนการแกสลิฟเคชันชีวมวลเป็นเทคโนโลยีหนึ่งที่สามารถผลิตแก๊สผลิตภัณฑ์ที่มี CO และ H₂ เป็นองค์ประกอบหลักซึ่งสามารถนำไปใช้ประโยชน์ได้อย่างกว้างขวาง อย่างไรก็ตามในการนำแก๊สผลิตภัณฑ์จากกระบวนการดังกล่าวมาใช้ประโยชน์มักประสบกับปัญหาเกี่ยวกับสารประกอบทาร์ซึ่งเป็นสารประกอบอินทรีย์ที่มีมวลโมเลกุลสูงและสามารถควบแน่นเป็นของเหลวที่อุณหภูมิต่ำ จึงจำเป็นต้องมีกระบวนการปรับปรุงแก๊สผลิตภัณฑ์โดยใช้ตัวเร่งปฏิกิริยาสำหรับกระบวนการแกสลิฟเคชันชีวมวล ในงานวิจัยนี้เป็นการศึกษาและปรับปรุงตัวเร่งปฏิกิริยาที่สามารถกำจัดสารประกอบทาร์โดยใช้ตัวเร่งปฏิกิริยาซีเรีย-เซอร์โคเนียสำหรับปฏิกิริยาออกซิเดชันและโดยใช้ตัวเร่งปฏิกิริยาโลหะนิกเกิลที่มีซีเรีย-เซอร์โคเนียเป็นตัวรองรับสำหรับปฏิกิริยารีฟอร์มมิงด้วยน้ำ จากการศึกษาค้นพบว่าตัวเร่งปฏิกิริยาซีเรีย-เซอร์โคเนียที่มีแมงกานีสเป็นตัวปรับปรุงคุณสมบัติ (Ce_{0.75}Zr_{0.15}Mn_{0.10}O₂) ให้ค่ากัมมันตภาพ (activity) สูงที่สุดสำหรับปฏิกิริยาออกซิเดชันของเบนซีน โทลูอิน และเนฟทาลีน และจากการศึกษาจลนพลศาสตร์ (kinetics) ของปฏิกิริยาออกซิเดชันของเนฟทาลีนโดยใช้ตัวเร่งปฏิกิริยาซีเรีย-เซอร์โคเนียพบว่าสามารถใช้กลไกของ Mars-van Krevelen อธิบายปฏิกิริยาดังกล่าวได้ จึงสรุปได้ว่ากัมมันตภาพของตัวเร่งปฏิกิริยาซีเรีย-เซอร์โคเนียสัมพันธ์กับคุณสมบัติทางรีดอกซ์ (redox property) สำหรับปฏิกิริยารีฟอร์มมิงด้วยน้ำนั้นจากการศึกษาค้นพบว่าตัวเร่งปฏิกิริยานิกเกิลบนตัวรองรับซีเรีย-เซอร์โคเนียที่มีแมงกานีสเป็นตัวปรับปรุงคุณสมบัติ (Ni/Ce_{0.75}Zr_{0.25-x}Mn_xO₂) และตัวเร่งปฏิกิริยานิกเกิลบนตัวรองรับชนิดซีเรีย-เซอร์โคเนียที่มีโลหะออกไซด์ได้แก่ โครเมียม (Cr) เหล็ก (Fe) แมงกานีส (Mn) และวานาเดียม (V) เป็นตัวปรับปรุงคุณสมบัติ (Ni/Ce_{0.75}Zr_{0.15}Me_{0.10}O₂ (Me = Cr, Fe, Mn และ V)) ให้ค่ากัมมันตภาพและเสถียรภาพ (stability) ที่สูงในช่วงเวลาที่ทำการศึกษาสำหรับปฏิกิริยารีฟอร์มมิงของโทลูอินและเนฟทาลีนด้วยน้ำ พบว่าในกรณีที่ใช้แมงกานีสสามารถรักษาหรือปรับปรุงคุณสมบัติทางรีดอกซ์ของตัวรองรับซีเรีย-เซอร์โคเนียโดยช่วยลดการเกิดคาร์บอนบนตัวเร่งปฏิกิริยาโดยเฉพาะป้องกันการเกิดคาร์บอนชนิดฟิลาเมนต์ (filamentous carbon) อีกด้วย

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