

**ROLES OF Zn SPECIES IN Zn-PROMOTED HZSM-5 CATALYSTS  
ON THE AROMATIZATION ACTIVITY**

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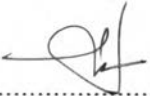
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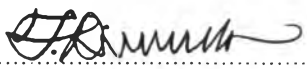
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## ABSTRACT

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The roles of Zn species in Zn/HZSM-5 catalyst on the aromatization of palm fatty acid distillate (PFAD), glycerol, and *n*-pentane were investigated. The amounts of Zn loading and preparation methods strongly affect the Zn species on HZSM-5 support. The Zn species strongly depended on the method of introducing Zn. Compared with ZnO, the higher dehydrogenation activity of  $(\text{ZnOH})^+$  showed the higher aromatization of glycerol. However, using PFAD as a feedstock, even the  $(\text{ZnOH})^+$  species is essential for improving the aromatization. The ZnO also plays a key role in the deoxygenation of PFAD, shifting the deoxygenation pathway from decarbonylation on Brønsted acid site to decarboxylation on ZnO, thus preserving the Brønsted acid site for aromatization. The evolution of Zn species upon different thermal treatments was studied by XPS and IPA-TPD. Under  $\text{H}_2$  atmosphere, hydrodehydroxylation of  $(\text{ZnOH})^+$  species generated  $(\text{ZnH})^+$ , further dissociated  $\text{H}_2$  molecule, forming  $(\text{ZnH}_3)^+$  species. The presence of  $(\text{ZnH}_3)^+$  was found to improve the aromatics selectivity. Even the  $(\text{ZnH}_3)^+$  species is not stable, it can be recovered upon  $\text{H}_2$  treatment. In order to improve the *p*-xylene selectivity, silicalite-1 was later coated on Zn/HZSM-5 catalyst. Even the selectivity of *p*-xylene was improved, the aromatics yield was found to be traded with *p*-xylene selectivity. To increase aromatics yield, Zn(II) ions were grafted on silicalite-1 layer. Due to its high dehydrogenation activity, *n*-pentane feedstock was firstly converted to olefins on Zn(II) ions/Sil-1 then further aromatized in Zn/HZSM-5 catalyst, thus improving *p*-xylene yield.

## บทคัดย่อ

ศิขริน เตมียกุล : บทบาทของสังกะสีแต่ละสปีชีส์บนตัวเร่งปฏิกิริยาแซทเอสเอ็ม-5 ที่ได้รับการเติมแต่งสังกะสี ต่อการเกิดปฏิกิริยาอะโรมาไทเซชัน (Roles of Zn Species in Zn-Promoted HZSM-5 Catalysts on the Aromatization Activity)

อาจารย์ที่ปรึกษา : รศ. ดร. ศิริพร จงผาทิวฒิ รศ. ดร. ตะวัน สุขน้อย

และ ศ. ดร. ลานซ์ แอล ลีอบแบน 126 หน้า

งานวิจัยนี้ศึกษาบทบาทของสังกะสีแต่ละสปีชีส์บนตัวเร่งปฏิกิริยาแซทเอสเอ็ม-5 ที่ได้รับการเติมแต่งสังกะสีต่อการเปลี่ยน กลีเซอรอล กรดไขมันปาล์ม และเอ็นเพนเทน เป็นสารอะโรมาติกส์ จากการทดลองพบว่า วิธีการเตรียมตัวเร่งปฏิกิริยาส่งผลต่อการเกิดสปีชีส์ที่แตกต่างกันของสังกะสี ในปฏิกิริยาอะโรมาไทเซชัน สังกะสีที่มีสปีชีส์เป็น  $(\text{ZnOH})^+$  มีความว่องไวและความเจาะจงในการเกิดสารอะโรมาติกส์สูงกว่า  $\text{ZnO}$  อย่างไรก็ตามเมื่อใช้กรดไขมันปาล์มเป็นสารตั้งต้นพบว่า ตัวเร่งปฏิกิริยาที่ประกอบด้วยสังกะสีทั้งสองสปีชีส์ส่งผลให้อัตราการเกิดผลิตภัณฑ์อะโรมาติกส์สูงขึ้น โดย  $(\text{ZnOH})^+$  ช่วยเร่งปฏิกิริยาอะโรมาไทเซชัน ในขณะที่  $\text{ZnO}$  ช่วยเร่งกระบวนการดีออกซิเจนชันผ่านปฏิกิริยาดีคาร์บอกซิเลชัน การศึกษาผลของการให้ความร้อนภายใต้แก๊สไฮโดรเจนของตัวเร่งปฏิกิริยาสังกะสีบนแซทเอสเอ็ม-5 พบว่าปฏิกิริยาไฮโดรดีไฮดรอกซิเลชันระหว่าง  $(\text{ZnOH})^+$  และแก๊สไฮโดรเจนทำให้ สปีชีส์ของสังกะสีเกิดการเปลี่ยนแปลงจาก  $(\text{ZnOH})^+$  เป็น  $(\text{ZnH})^+$  ซึ่งภายใต้สภาวะที่มีแก๊สไฮโดรเจน การดูดซับทางเคมีของโมเลกุลไฮโดรเจนบน  $(\text{ZnH})^+$  ทำให้สปีชีส์ของสังกะสีเกิดการเปลี่ยนแปลงเป็น  $(\text{ZnH}_3)^+$  เมื่อเปรียบเทียบความว่องไวและความเจาะจงในการเกิดสารอะโรมาติกส์ของสังกะสีทั้งสามสปีชีส์พบว่า  $(\text{ZnH}_3)^+$  มีความสามารถสูงสุดในปฏิกิริยาอะโรมาไทเซชันของเอ็นเพนเทน ถึงแม้ว่าสปีชีส์ดังกล่าวจะไม่เสถียรในภาวะที่ปราศจากแก๊สไฮโดรเจน แต่สามารถเกิดขึ้นใหม่ได้โดยการให้ความร้อนภายใต้แก๊สไฮโดรเจน เพื่อเพิ่มความจำเพาะต่อการเกิดผลิตภัณฑ์พาราไซลีน ตัวเร่งปฏิกิริยาสังกะสีบนแซทเอสเอ็ม-5 ได้ถูกเคลือบด้วยซิลิกาไลต์-1 จากการปรับปรุงผิวด้านนอกของตัวเร่งปฏิกิริยาส่งผลให้ความจำเพาะต่อพาราไซลีนมากขึ้น แต่ความว่องไวในการเกิดปฏิกิริยาลดลง อย่างไรก็ตามหลังจากเติมสังกะสีลงบนผิวด้านนอกของซิลิกาไลต์-1 สปีชีส์ของสังกะสีที่เกิดขึ้นคือ  $\text{Zn(II)ions}$  ซึ่งมีความสามารถสูงในปฏิกิริยาดีไฮโดรจิเนชัน ส่งผลให้ตัวเร่งปฏิกิริยามีอัตราการเกิดปฏิกิริยาอะโรมาไทเซชันและความจำเพาะต่อพาราไซลีนสูงขึ้น

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