

**EFFECT OF SULFUR ON *n*-OCTANE AROMATIZATION OVER
Sn- AND Ge-PROMOTED Pt/KL CATALYSTS**



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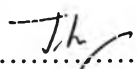
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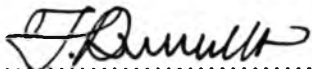
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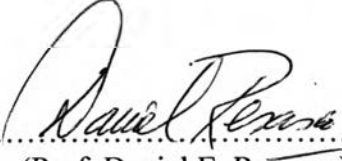

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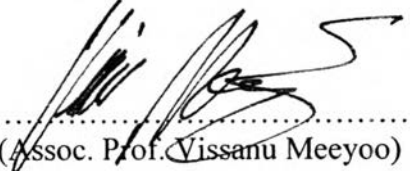
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ABSTRACT

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Pornpimon Paopahon: Effect of Sulfur on *n*-Octane Aromatization over Sn- and Ge-promoted Pt/KL Catalysts

Thesis Advisors: Asst. Prof. Siriporn Jongpatiwut, Assoc. Prof. Thirasak Rirksomboon, Prof. Somchai Osuwan, and Prof. Daniel E. Resasco 68 pp.

Keywords: *n*-Octane Aromatization/ Sulfur Tolerance/ Pt-Sn/ Pt-Ge/ Pt/KL Zeolite

In previous studies, it was found that PtSn/KL catalysts prepared by vapor-phase co-impregnation exhibit remarkably high stability and selectivity to C8-aromatics for *n*-octane aromatization. One of the serious drawbacks of Pt/KL-based catalysts is their high sensitivity to even traces of sulfur. The addition of Ge was found to improve sulfur tolerance of Pt/Al₂O₃ catalyst. In this work, the sulfur tolerance of Sn- and Ge-promoted Pt/KL catalysts, including the effects of varying Ge content, have been investigated. The catalysts prepared by vapor-phase co-impregnation were characterized by TPR, TPO, hydrogen chemisorptions, TEM, DRIFTS, and XPS. Reaction measurements were carried out at 500 °C and atmospheric pressure. It was found that, in the absence of sulfur, Pt-Sn/KL and Pt-Ge/KL could improve the catalytic activity and the selectivity to C8-aromatics compared with unpromoted Pt/KL catalyst. In the case of bimetallic Pt-Ge catalyst, the appropriate amount of Ge loading with 0.6 wt% Pt loading selected to prepare the catalyst was 0.6 wt%. In the presence of 25 ppm sulfur, the unpromoted Pt/KL catalyst for *n*-octane aromatization was not extremely high sensitivity to sulfur as much as for *n*-hexane aromatization. The sensitivity to sulfur was also found in the aromatization of *n*-octane on Pt-Ge/KL catalyst. By contrast, on the Pt-Sn/KL catalyst, the *n*-octane aromatization activity was not diminished by the presence of sulfur, but actually increased. TEM images displayed higher distributed metal clusters on Pt-Sn/KL and Pt-Ge/KL compared to the unpromoted Pt/KL catalyst.

บทคัดย่อ

พรพิมล เผ่าพหล : อิทธิพลของซัลเฟอร์ต่อปฏิกิริยาอะโรมาไทเซชันของนอร์มัลออกเทน โดยใช้ตัวเร่งปฏิกิริยาแพลตตินัมบนซีโอไลต์ที่เติมดีบุกหรือเจอร์เมเนียม (Effect of Sulfur on *n*-Octane Aromatization over Sn- and Ge-promoted Pt/KL Catalysts) อาจารย์ที่ปรึกษา : ผศ.ดร. ศิริพร จงผาคิวฒิ รศ.ดร. ชีรศักดิ์ ฤกษ์สมบูรณ์ ศ. สมชาย โอสุวรรณ และ ศ. แคนเน็ล อี ริชส์โก 68 หน้า

จากการศึกษาที่ผ่านมาพบว่าตัวเร่งปฏิกิริยา PtSn/KL ซึ่งเตรียมโดยวิธีการระเหิดสารประกอบแพลททินัมและดีบุกเข้าไปยังโพรงของซีโอไลต์มีความเสถียรและความเลือกเฉพาะกับผลิตภัณฑ์อะโรมาติกส์ที่มีคาร์บอน 8 อะตอมสูงสำหรับปฏิกิริยาอะโรมาไทเซชันของนอร์มัลออกเทน หนึ่งในข้อเสียของตัวเร่งปฏิกิริยาจำพวก Pt/KL คือการเสื่อมสภาพอย่างรวดเร็วในที่มีซัลเฟอร์ การเติม โลหะเจอร์เมเนียมลงบนตัวเร่งปฏิกิริยาแพลททินัมบนอะลูมินา (Pt/Al₂O₃) สามารถเพิ่มความทนทานต่อการเป็นพิษของซัลเฟอร์ของตัวเร่งปฏิกิริยาได้ ดังนั้นในงานวิจัยนี้จึงศึกษาความต้านทานต่อซัลเฟอร์ของตัวเร่งปฏิกิริยา Pt/KL ที่มีการเติมโลหะดีบุกและเจอร์เมเนียม รวมถึงผลของการเปลี่ยนแปลงปริมาณโลหะเจอร์เมเนียม เตรียมตัวเร่งปฏิกิริยาโดยวิธีการระเหิดสารประกอบเข้าไปยังโพรงซีโอไลต์และวิเคราะห์หาคุณสมบัติด้วยเทคนิคต่างๆ ได้แก่ ความสามารถในการดูดซับแก๊สไฮโดรเจน TPR TPO TEM DRIFTS และ XPS การทดสอบตัวเร่งปฏิกิริยาสำหรับการเร่งปฏิกิริยาอะโรมาไทเซชันของนอร์มัลออกเทนทำที่ 500 องศาเซลเซียส และความดันบรรยากาศ ผลการทดลองพบว่าสำหรับสารป้อนออกเทนที่ไม่มีซัลเฟอร์เจือ ตัวเร่งปฏิกิริยา Pt-Sn/KL และ Pt-Ge/KL เพิ่มความสามารถในการเกิดปฏิกิริยาและการเลือกเฉพาะกับผลิตภัณฑ์อะโรมาติกส์ให้สูงขึ้น นอกจากนี้พบว่าปริมาณเจอร์เมเนียมที่เหมาะสมกับการเกิดปฏิกิริยาคือร้อยละ 0.6 สำหรับกรณีที่สารป้อนออกเทนมีซัลเฟอร์เจือ ตัวเร่งปฏิกิริยา Pt/KL ไม่แสดงการเสื่อมอย่างเห็นได้ชัด ในขณะที่ตัวเร่งปฏิกิริยา Pt-Ge/KL แสดงการเสื่อมอย่างชัดเจนสำหรับตัวเร่งปฏิกิริยา Pt-Sn/KL นอกจากนี้ไม่เสื่อมสภาพอย่างรวดเร็วในที่มีซัลเฟอร์ ยังมีความสามารถในการเกิดปฏิกิริยาสูงขึ้นอีกด้วย รูปของ TEM แสดงให้เห็นการกระจายตัวได้ดีของโลหะบน Pt-Sn/KL และ Pt-Ge/KL เมื่อเทียบกับตัวเร่งปฏิกิริยา Pt/KL

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