

**TOLUENE ALKYLATION WITH METHANOL USING MODIFIED HZSM-5  
CATALYSTS : SILYLATION AND DEALUMINATION**

Nut Tangphianphan

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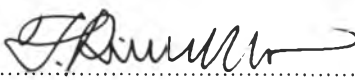
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Asst. Prof. Siriporn Jongpatiwut

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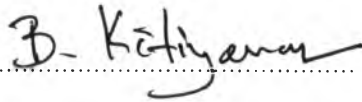
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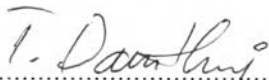
  
..... College Dean  
(Asst. Prof. Pomthong Malakul)

**Thesis Committee:**

  
.....  
(Assoc. Prof. Thirasak Rirksomboon)

  
.....  
(Asst. Prof. Siriporn Jongpatiwut)

  
.....  
(Asst. Prof. Boonyarach Kitiyanan)

  
.....  
(Dr. Tanate Danuthai)

## ABSTRACT

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*p*-Xylene is the most important intermediate in xylene isomers. It is mainly used for producing terephthalic acid. Currently, *p*-xylene is produced by disproportionation of toluene and *p*-xylene-oriented isomerization of mixed xylene isomers. However, these processes will produce a large quantity of benzene, hence, the cost of isolation and purification is relatively high. The catalytic methylation of toluene is, therefore, a very promising alternative method of producing *p*-xylene without any by-product. A variety of zeolites have been used for catalyzing this reaction such as acidic zeolite, HZSM-5 because of its suitable pore size for *p*-xylene diffusion. On the other hand, the acid sites on the external catalyst surface would cause an isomerization of *p*-xylene to *o*- and *m*-xylene, resulting in decreasing the selectivity to *p*-xylene. The purpose of this study was to deactivation of its external acid sites. The HZSM-5 catalysts used were modified via i) chemical liquid deposition (CLD), and ii) dealumination via acid treatment. The varied amounts and cycles of tetraethyl orthosilicate (TEOS) loading in the ranges of, 0.5-2.0 ml.g<sup>-1</sup> and 1-3 times respectively, were employed for the former method whereas the use of 0.5 M oxalic acid was for the latter. Catalytic activity testing was carried out at atmospheric pressure, 400 °C, WHSV of 24 h<sup>-1</sup>, and toluene to methanol ratio of 4. The results showed that the catalyst modified via the CLD with a TEOS concentration of 1 ml/g.cat. with 2-cycle treatment exhibited the highest *p*-xylene selectivity in product from 67.29 % to 84.39 % or *p*-xylene selectivity in xylene from 75.17 % to 92.05 % as compared to the parent catalyst.

## บทคัดย่อ

ณัฐ ตั้งเพียรพันธ์ : ปฏิริยาแอลคิเลชันของโทลูอินกับเมทานอลโดยใช้ตัวเร่งปฏิริยาซีโอไลท์ที่ได้รับการปรับแต่งชนิด HZSM-5 โดยวิธีไซลิเลชัน และ ดีอะลูมิเนชัน (Toluene Alkylation with Methanol using Modified HZSM-5 Catalysts: Silylation Dealumination) อ. ที่ปริศึกษา : รศ. ดร. ชีรศักดิ์ ฤกษ์สมบูรณ์ และ ผศ.ดร. ศิริพร จงผาดิวุฒิ 63 หน้า

ไซลีน โดยเฉพาะพาราไซลีนเป็นสารตั้งต้นที่สำคัญในการผลิตกรดเทอเรพทาลิกและไดเมทิลเทอเรพทาลิก ในปัจจุบันพาราไซลีนผลิตโดยปฏิริยาดีสพรอพอชันเนชันของโทลูอินและปฏิริยาไอโซเมอร์ไรเซชันของสารผสมไซลีน แต่อย่างไรก็ตามปฏิริยาที่กล่าวมานี้ผลิตเบนซีนออกมาในปริมาณมาก เพราะเหตุนี้ต้นทุนในกระบวนการแยกและการทำให้สารบริสุทธิ์นั้นมีราคาค่อนข้างสูง ด้วยเหตุนี้กระบวนการแอลคิเลชันของโทลูอินกับเมทานอลจึงเป็นทางเลือกในการผลิตพาราไซลีนโดยใช้ตัวเร่งปฏิริยาซีโอไลท์ชนิดต่างๆ โดยซีโอไลท์ชนิดต่างๆถูกใช้ในการเป็นตัวเร่งปฏิริยาในกระบวนการแอลคิเลชัน ในการทดลองนี้ได้เลือกใช้ซีโอไลท์ชนิด HZSM-5 เนื่องจากมีขนาดรูพรุนที่เหมาะสมกับขนาดโมเลกุลของพาราไซลีนที่แพร่ออกมา แต่เนื่องจากพื้นผิวที่เป็นกรดบนผิวด้านนอกของซีโอไลท์สามารถทำให้เกิดปฏิริยาไอโซเมอร์ไรเซชันของพาราไซลีนเป็นไซลีนชนิดอื่นๆได้ ดังนั้นงานวิจัยนี้จึงได้ทำการศึกษาปฏิริยาแอลคิเลชันของโทลูอินกับเมทานอลบนตัวเร่งปฏิริยาซีโอไลท์ชนิด HZSM-5 โดยทำการปรับแต่งด้วยวิธีการ 1) ปรับปรุงพื้นผิวด้วยของเหลวเชิงเคมี(chemical liquid deposition)(CLD) 2) การลดปริมาณอะลูมิเนียม(dealumination) ที่พื้นผิวด้วยเร่งปฏิริยาโดยใช้กรด สำหรับวิธีการแรกทำการปรับเปลี่ยนปริมาณและจำนวนรอบในการปรับปรุงพื้นผิวด้วยเทระเอซิลออโทริซิลิเกต (TEOS) โดยการปรับเปลี่ยนปริมาณในช่วง 0.5-2.0 มิลลิลิตรต่อกรัม และจำนวนรอบ 1-3 รอบ ส่วนในวิธีการที่สองใช้กรดออกซาลิกความเข้มข้น 0.5 โมล โดยอัตราการเกิดปฏิริยาผ่านตัวเร่งได้ถูกทดสอบภายใต้สภาวะบรรยากาศ ที่อุณหภูมิในการทำปฏิริยา 450 องศาเซลเซียส อัตราการไหล (WHSV) ที่ 24 ต่อชั่วโมง และอัตราส่วนโทลูอินต่อเมทานอลเท่ากับ 4 โดยใช้ปฏิริยาแบบเบดนิ่ง จากผลการทดลองแสดงให้เห็นว่ากรดซีโอไลท์ชนิด HZSM-5 ที่ผ่านการทำ CLD ที่ 2 รอบโดยใช้ TEOS ให้ผลการเลือกเกิดพาราไซลีนในผลิตภัณฑ์จาก 67.29% เป็น 84.39% หรือการเลือกเกิดพาราไซลีนในไซลีนจาก 75.17 % to 92.05 % เมื่อเปรียบเทียบกับ HZSM-5 ที่ยังไม่ได้ถูกดัดแปลง

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