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จุฬาลงกรณ์มหาวิทยาลัย

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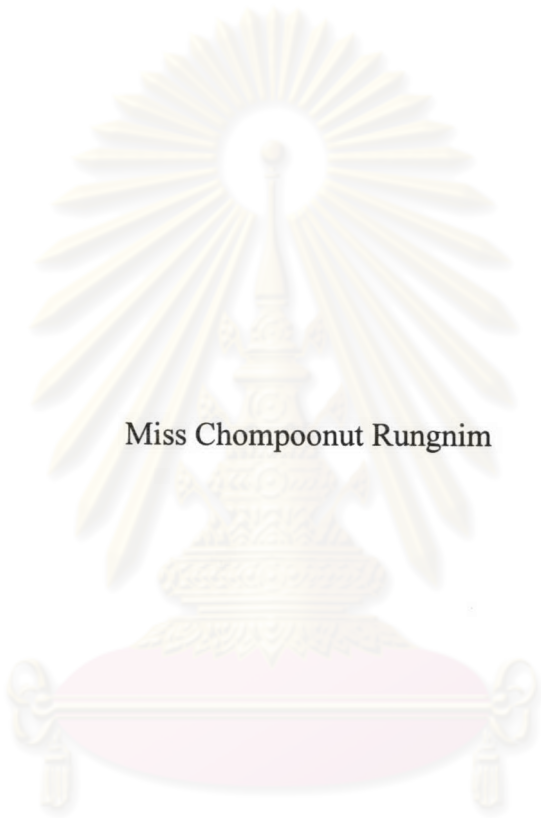
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THEORETICAL STUDY OF PINACOL REARRANGEMENT USING
ACID-CATALYZED SYSTEM AND ZSM-5



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ศูนย์วิทยทรัพยากร
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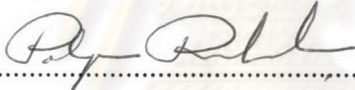
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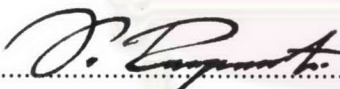
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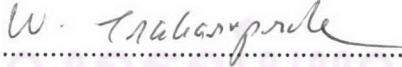
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ชมพูนุช รุ่งน้อม : การศึกษาเชิงทฤษฎีของการจัดตัวใหม่แบบพินาคอลโดยใช้ระบบเร่งปฏิกิริยาด้วยกรดและแซคเอสเอ็ม-5. (THEORETICAL STUDY OF PINACOL REARRANGEMENT USING ACID-CATALYZED SYSTEM AND ZSM-5) อ. ที่ปรึกษา : รศ. ดร. วิทยา เรืองพรวิสุทธิ์, 129 หน้า. ISBN 974-17-4615-6.

ศึกษาการจัดตัวใหม่แบบพินาคอลโดยใช้ระบบเร่งปฏิกิริยาด้วยกรด แซคเอสเอ็ม-5 และโมเลกุลอาชีพที่แทนที่ด้วยโลหะด้วยการคำนวณทางทฤษฎีเคมีที่ฟังก์ชันโดยวิธี B3LYP/6-31G (d) ตัวเร่งปฏิกิริยาแซคเอสเอ็ม-5 จำลองโครงสร้างด้วยโมเดล 3T และ 5T สำหรับโมเลกุลอาชีพที่แทนที่ด้วยโลหะที่นำมาเป็นตัวอย่างในการศึกษาคือเหล็ก Fe(II) และทองแดง Cu(II) ที่แทนที่ในโครงสร้างซีโอไลต์ โดยจำลองโครงสร้างด้วยโมเดล Fe-3T และ Cu-3T ผลการศึกษาพบว่าค่าพลังงานกระตุ้นของปฏิกิริยาการจัดตัวใหม่แบบพินาคอลที่คำนวณจากโมเดล Fe-3T และ Cu-3T มีค่า 29.63 และ 37.11 กิโลแคลอรีต่อโมลตามลำดับ แสดงให้เห็นว่าเหล็กที่แทนที่ในโครงสร้างของซีโอไลต์มีสมบัติในการเร่งปฏิกิริยาการจัดตัวใหม่แบบพินาคอลดีกว่าทองแดง นอกจากนี้ได้ศึกษาปฏิกิริยาการจัดตัวใหม่แบบพินาคอลของโพรพิลีนไกลคอลเพื่อเปลี่ยนเป็นโพรพานอลและโพรพานอน ซึ่งเกิดผ่านสภาวะแทรนซิชัน 3 สภาวะคือ TS1, TS2 และ TS3 โดยใช้ระบบเร่งปฏิกิริยาแบบกรดและซีโอไลต์ เพื่อเปรียบเทียบอัตราส่วนของผลิตภัณฑ์สำหรับระบบเร่งปฏิกิริยาด้วยกรด ได้ศึกษาด้วยโมเดลที่มีโมเลกุลของน้ำเพิ่มขึ้นสี่โมเดลคือ โมเดล I ถึงโมเดล IV พบว่าจำนวนโมเลกุลของน้ำที่ล้อมรอบในสภาวะแทรนซิชันทั้งสามส่งผลต่ออัตราส่วนของผลิตภัณฑ์ การประมาณค่าเปอร์เซ็นต์อัตราส่วนผลิตภัณฑ์คำนวณได้จากค่าพลังงานกระตุ้นอิสระของแต่ละโมเดล โดยเปอร์เซ็นต์อัตราส่วนผลิตภัณฑ์ระหว่างโพรพานอลกับโพรพานอนที่คำนวณจากโมเดล I, II, III และ IV มีค่าเท่ากับ [99.88]:[0.12], [99.81]:[0.19], [89.01]:[10.99] และ [46.59]:[53.41] ตามลำดับ ในขณะที่เปอร์เซ็นต์อัตราส่วนผลิตภัณฑ์ระหว่างโพรพานอลกับโพรพานอนที่คำนวณจากโมเดล 3T และ 5T มีค่าเท่ากับ [2.36]:[97.64] และ [2.56]:[97.44] ตามลำดับ

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต 

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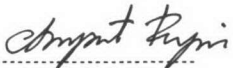

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CHOMPOONUT RUNGNIM : THEORETICAL STUDY OF PINACOL
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THESIS ADVISOR : ASSOC. PROF. VITHAYA RUANGPORNVISUTI,
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Pinacol rearrangements using acid-catalyzed system, ZSM-5 and metal substituted molecular sieve catalyst have been investigated using density functional theory method at B3LYP/6-31G(d) level of theory. The ZSM-5 catalyst was modeled as 3T and 5T cluster models. The metal substituted molecular sieves represented by Fe(II) and Cu(II) substituted in zeolite framework were modeled using Fe-3T and Cu-3T cluster models. The results show that activation energies of pinacol rearrangement over Fe-3T and Cu-3T are 29.63 and 37.11 kcal/mol, respectively. As a result, Fe substituted in framework of zeolite presents higher catalytic activity for pinacol rearrangement than Cu substituted in zeolite framework. Moreover, the pinacol rearrangements of propylene glycol conversion to propanal and propanone via transition states TS1, TS2 and TS3 have been investigated using acid-catalyzed system and ZSM-5 in order to compare the product distribution ratio. In the acid-catalyzed system, the four water-addition models I to IV, were obtained. The number of hydration water interacting with the transition states of three concerted pathways has obviously affected the product ratio. Estimated percentages of product composition computed from activation free energies of each reaction models were carried out. The percent ratios of product propanal to propanone based on models I, II, III and IV are [99.88]:[0.12], [99.81]:[0.19], [89.01]:[10.99] and [46.59]:[53.41], respectively while the percent ratios of product propanal to propanone based on 3T and 5T cluster models are [2.36]:[97.64] and [2.56]:[97.43], respectively.

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ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

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