

**CATALYTIC EPOXIDATION OF CYCLOHEXENE OVER DIFFERENT
OXIDE CATALYSTS**



Kittisak Woragamon

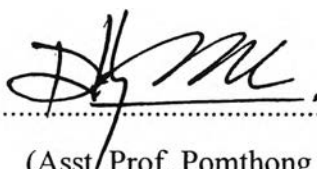
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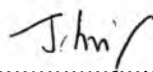
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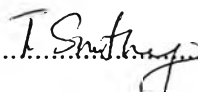
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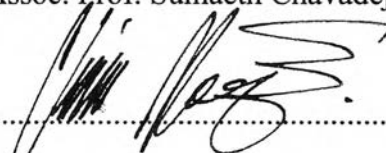
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ABSTRACT

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Cyclohexene oxide is an important intermediate in several chemical industries. It can be produced via partial oxidation of cyclohexene, so-called cyclohexene epoxidation. Many research works have been focused on the development of new active and selective catalysts for cyclohexene epoxidation that can avoid undesired reactions. The purpose of this work is to investigate the cyclohexene epoxidation using different catalysts, i.e. commercial TiO₂ (TiO₂ (P-25)), sol-gel-synthesized mesoporous-assembled TiO₂ (TiO₂ (SG)), SiO₂, Al₂O₃, and Fe₃O₄. The experimental results showed that TiO₂ (SG) provided the highest cyclohexene conversion and cyclohexene oxide selectivity. The addition of RuO₂ is investigated on TiO₂ (SG) prepared by two methods: (1) incipient wetness impregnation (IWI) method (RuO₂/TiO₂ (IWI)) and (2) single-step sol-gel (SSSG) method (RuO₂/TiO₂ (SSSG)). Between RuO₂/TiO₂ (IWI) and RuO₂/TiO₂ (SSSG), 1 mol% RuO₂/TiO₂ (IWI) calcined at 550°C for 4 h was found to possess selectively high catalytic performance based on cyclohexene oxide production. The optimum reaction conditions found are H₂O₂-to-cyclohexene ratio of 1, *t*-butanol as solvent, catalyst amount of 0.5 g, and reaction temperature of 70°C. The recyclability of the RuO₂/TiO₂ (IWI) and RuO₂/TiO₂ (SSSG) catalysts is also investigated. It was found that after three cycles, RuO₂/TiO₂ (IWI) exhibits slight decrease in cyclohexene conversion with significant decrease in cyclohexene oxide selectivity. On the other hand, RuO₂/TiO₂ (SSSG) exhibits almost unchanged in both conversion and selectivity, indicating its higher stability.

บทคัดย่อ

กิตติศักดิ์ วรกมล : ปฏิกริยาอ็อกซิเดชันของไซโคลเฮกซีน โดยใช้โลหะออกไซด์เป็นตัวเร่งปฏิกิริยา (Catalytic Epoxidation of Cyclohexene over Different Oxide Catalysts)
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ไซโคลเฮกซีนออกไซด์ เป็นสารมัธยันต์ที่สำคัญและมีประโยชน์สำหรับกระบวนการอุตสาหกรรมเคมี ซึ่งสามารถสังเคราะห์ได้โดยปฏิกิริยาอ็อกซิเดชันของไซโคลเฮกซีน ดังนั้นนักวิจัยจึงมีความพยายามที่จะพัฒนาตัวเร่งปฏิกิริยาให้มีความสามารถในการเร่งปฏิกิริยาและความจำเพาะเจาะจงในการเลือกเกิดผลิตภัณฑ์ สำหรับปฏิกิริยาอ็อกซิเดชันของไซโคลเฮกซีนเพื่อที่จะหลีกเลี่ยงการเกิดปฏิกิริยาข้างเคียงซึ่งส่งผลต่อการเกิดผลิตภัณฑ์ที่ไม่ต้องการ ด้วยเหตุนี้วัตถุประสงค์ของงานวิจัยนี้ คือ ทำการศึกษาปฏิกิริยาอ็อกซิเดชันของไซโคลเฮกซีน โดยการใช้ตัวเร่งปฏิกิริยาหลายชนิด ได้แก่ ไทเทเนียมที่ใช้ในเชิงทางการค้า, ไทเทเนียมที่ได้จากการสังเคราะห์โดยวิธีโซลเจล, ซิลิกา, อลูมินา, และ แมกนีไทด์ จากการทดลองแสดงให้เห็นว่า ไทเทเนียมที่ได้จากการสังเคราะห์นั้น เป็นตัวรองรับที่ดีที่สุดเนื่องจากทำให้ได้ค่าการเปลี่ยนแปลงของไซโคลเฮกซีนและ ค่าการเลือกเกิดของไซโคลเฮกซีนออกไซด์มากที่สุด การเติมรูเทเนียมไดออกไซด์บนพื้นผิวของไทเทเนียมที่ได้จากการสังเคราะห์ถูกเตรียมโดยวิธีการฝังตัวแบบแห้งและโซลเจลแบบขั้นตอนเดียว ซึ่งจากผลการเปรียบเทียบพบว่า รูเทเนียมไดออกไซด์ปริมาณ 1 โมลเปอร์เซ็นต์ บนพื้นผิวไทเทเนียม ที่ถูกเตรียมโดยวิธีการฝังตัวแบบแห้งและเผาที่อุณหภูมิ 550 องศาเซลเซียส เป็นเวลา 4 ชั่วโมง นั้นเป็นตัวเร่งปฏิกิริยาที่เหมาะสมที่สุดเนื่องจากมีประสิทธิภาพในการเร่งปฏิกิริยาสูงสุดเมื่อพิจารณาจากค่าการเลือกเกิดของไซโคลเฮกซีนออกไซด์ สภาวะของปฏิกิริยาที่เหมาะสมที่สุด ได้แก่ อัตราส่วนระหว่างไฮโดรเจนเปอร์ออกไซด์ต่อไซโคลเฮกซีน = 1, ปริมาณตัวเร่งปฏิกิริยา = 0.5 กรัม, อุณหภูมิในการทำปฏิกิริยา = 70 องศาเซลเซียส ยิ่งไปกว่านั้นยังได้ศึกษาการนำตัวเร่งปฏิกิริยากลับมาใช้ใหม่เป็นจำนวน 3 ครั้งต่อเนื่อง ซึ่งผลจากการศึกษาพบว่า ค่าการเปลี่ยนแปลงของไซโคลเฮกซีน มีค่าลดลงเล็กน้อย แต่ ค่าการเลือกเกิดของไซโคลเฮกซีนออกไซด์ มีค่าลดลงอย่างมาก เมื่อใช้รูเทเนียมไดออกไซด์บนไทเทเนียมที่ถูกเตรียมโดยวิธีการฝังตัวแบบแห้ง ในทางตรงข้าม รูเทเนียมไดออกไซด์บนไทเทเนียมที่ถูกเตรียมโดยวิธีโซลเจลแบบขั้นตอนเดียวมีความเสถียรมากกว่าเนื่องจากมีค่าการเปลี่ยนแปลงของไซโคลเฮกซีน และ ค่าการเลือกเกิดของไซโคลเฮกซีนออกไซด์ น้อยเมื่อเทียบกับผลที่ได้จากการทำปฏิกิริยาครั้งแรก

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