

**METHYL BROMIDE SYNTHESIS  
VIA OXIDATIVE BROMINATION OF METHANE**


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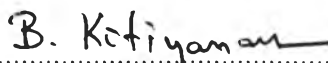
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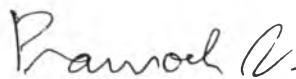


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## ABSTRACT

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The thermodynamic stability of methane is a critical factor for methane utilization. Oxidative bromination of methane (OBM) is one of the reaction pathways to transform methane into more reactive reactant, methyl bromide (CH<sub>3</sub>Br), which can be used for the productions of higher hydrocarbons and/or other compounds. In the current study, methane was brominated with HBr/H<sub>2</sub>O, with the flow of oxygen and nitrogen in a fixed-bed continuous-flow reactor at atmospheric pressure. The effect of various parameters including support materials, wt% Rh/SiO<sub>2</sub> catalyst, reaction temperature, and %O<sub>2</sub> were investigated. Before and after the reaction, the catalysts were also characterized by several techniques—BET, XRD, TPR, H<sub>2</sub> Chemisorption, and SEM. The results shows that under the same conditions (20 ml/min of CH<sub>4</sub>, 5 ml/min of O<sub>2</sub>, 5 ml/min of N<sub>2</sub>, 6.5 ml/h of 48 wt% HBr/H<sub>2</sub>O), high selectivity of CH<sub>3</sub>Br (100%) could be achieved at reaction temperature of 400°C, while at higher temperature partial oxidation of methane to synthesis gas was instead dominant. Moreover, when adding Rh/SiO<sub>2</sub> catalyst, the methane conversion increased while the high selectivity to methyl bromide was preferable.

## บทคัดย่อ

วาริณี ศิริจันทร์รัตน์ : การสังเคราะห์เมทิลโบรไมด์ด้วยปฏิกิริยาออกซิเดทีฟโบรมิเนชันของมีเทน (Methyl Bromide Synthesis via Oxidative Bromination of Methane) อาจารย์ที่ปรึกษา : ผศ. ดร. บุนยรัชต์ กิตยานันท์ 77 หน้า

ความเสถียรทางเทอร์โมไดนามิกส์ของมีเทนเป็นอุปสรรคที่สำคัญต่อการนำมีเทนไปใช้ในทางอุตสาหกรรมต่างๆ ปฏิกิริยาออกซิเดทีฟโบรมิเนชันของมีเทนเป็นอีกทางเลือกหนึ่งในการเปลี่ยนสารตั้งต้นมีเทนไปเป็นรูปที่ว่องไวต่อการเกิดปฏิกิริยามากยิ่งขึ้น เมทิลโบรไมด์ซึ่งเป็นผลิตภัณฑ์หลักที่ได้จากปฏิกิริยาดังกล่าว สามารถนำไปเป็นสารตั้งต้นในการผลิตสารประกอบไฮโดรคาร์บอนมวลโมเลกุลสูง หรือสารประกอบอื่นๆอีกมากมาย ในการทดลองนี้มีเทนจะทำปฏิกิริยากับแก๊สออกซิเจนและกรดไฮโดรโบรมิกโดยมีแก๊สไนโตรเจนเป็นตัวพา สารตั้งต้นทั้งหมดจะถูกป้อนสู่เตาปฏิกรณ์แบบต่อเนื่องและทำปฏิกิริยาที่ความดันบรรยากาศ นอกจากนี้แล้วในการทดลองยังมีการหาสภาวะที่เหมาะสมของตัวแปรต่างๆ อันได้แก่ ชนิดของตัวรองรับ อุณหภูมิที่ใช้ในการทำปฏิกิริยา ปริมาณโลหะโรเดียม และปริมาณออกซิเจนที่ใช้ โดยก่อนและหลังการทำปฏิกิริยา ตัวเร่งปฏิกิริยาจะถูกวิเคราะห์ด้วยเทคนิคต่างๆ เพื่อหาพื้นที่ผิว ความเป็นผลึก รูปร่างไอออนของโลหะ การกระจายตัวของโลหะและโครงสร้างระดับพื้นผิว จากผลการทดลองพบว่าที่สภาวะการทดลองเดียวกัน (20 มิลลิลิตรต่อนาทีของมีเทน, 5 มิลลิลิตรต่อนาทีของออกซิเจน, 5 มิลลิลิตรต่อนาทีของไนโตรเจน และ 6.5 มิลลิลิตรต่อชั่วโมงของกรดไฮโดรโบรมิก) ค่าการเลือกเกิดของเมทิลโบรไมด์ที่เท่ากับ 100% สามารถทำได้โดยใช้อุณหภูมิการทำปฏิกิริยาเท่ากับ 400 องศาเซลเซียส และพบว่ายิ่งอุณหภูมิการทำปฏิกิริยาสูงขึ้น จะไปสนับสนุนให้เกิดปฏิกิริยาออกซิเดชันของมีเทนเพื่อเปลี่ยนไปเป็นแก๊สสังเคราะห์แทน การนำตัวเร่งปฏิกิริยาของโลหะโรเดียมบนตัวรองรับซิลิกามาใช้จะช่วยปรับปรุงค่าการแปลงผันของมีเทนให้เพิ่มขึ้น โดยที่ค่าการเลือกเกิดของเมทิลโบรไมด์ยังอยู่ในเกณฑ์ที่น่าพอใจ

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