

**DIETHYL CARBONATE SYNTHESIS FROM ETHANOL AND LIQUID
CARBON DIOXIDE IN SUPERCRITICAL CONDITION OVER CeO₂-ZrO₂
CATALYSTS**


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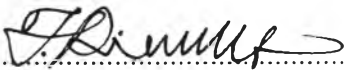
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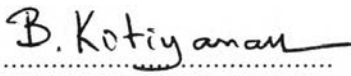

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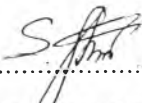
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ABSTRACT

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Danuwat Bunstapornpipat: Diethyl Carbonate Synthesis from Ethanol and Liquid Carbon Dioxide in Supercritical Condition over CeO₂-ZrO₂ Catalysts.

Thesis Advisors: Assoc. Prof. Thirasak Rirksomboon, Asst. Prof. Siriporn Jongpatiwut, and Asst. Prof. Thammanoon Sreethawong 68 pp.

Keywords: Diethyl carbonate/ Supercritical carbon dioxide/ Ethanol/ Ceria-zirconia mixed oxide catalyst

The synthesis of diethyl carbonate (DEC) from ethanol (EtOH) and liquid carbon dioxide (CO₂) in supercritical condition over ceria-zirconia mixed oxides (CeO₂-ZrO₂) catalysts using a high-pressure batch reactor system was studied by varying reaction temperatures from 110 to 170 °C, reaction time from 0 to 8 h, and CO₂/EtOH feed molar ratios at 1:1, 2:1, and 4:1. The catalysts were prepared by co-precipitation method followed by calcination at 500 or 700 °C, with percentages by mole of Ce in the mixed oxides at 0, 7, 20, and 40. The catalysts were characterized by TG-DTA, XRD, BET, and TPD. The results revealed that the Ce_{0.07}Zr_{0.93}O₂ calcined at a temperature of 700 °C operated at a feed molar ratio of 1:1, a reaction temperature at 140 °C, and a reaction time of 8 h, gave the highest catalytic activity resulting in DEC selectivity of 97.5%. The presume of tetragonal phase and weak acid-base properties of the Ce_{0.07}Zr_{0.93}O₂ were essential for the synthesis of DEC. By comparison between supercritical and gas phase conditions used for the synthesis, it was found that the amount of DEC produced could be enhanced when operated in supercritical condition.

บทคัดย่อ

คุณวรรณ บุญสถาพรพิพัฒน์ : การสังเคราะห์ไดเอทิลคาร์บอเนตจากเอทานอลและคาร์บอนไดออกไซด์เหลวภายใต้สภาวะเหนือวิกฤตด้วยตัวเร่งปฏิกิริยาซีเรีย-เซอโคเนียออกไซด์ (Diethyl Carbonate Synthesis from Ethanol and Liquid Carbon Dioxide in supercritical condition over $\text{CeO}_2\text{-ZrO}_2$ Catalysts) อ. ที่ปรึกษา : รศ.ดร. ชีรศักดิ์ ฤกษ์สมบูรณ์ ผศ.ดร. ศิริพร จงผาคิวุฒิ และ ผศ.ดร. ชรรมนุญ ศรีทะวงศ์ 68 หน้า

การสังเคราะห์ไดเอทิลคาร์บอเนตจากเอทานอลและคาร์บอนไดออกไซด์เหลวภายใต้สภาวะเหนือวิกฤตด้วยตัวเร่งปฏิกิริยาซีเรียซีเรีย-เซอโคเนียออกไซด์ในระบบเครื่องปฏิกรณ์ความดันสูงแบบกะ ได้รับการศึกษาโดยการเปลี่ยนแปลงอุณหภูมิที่ใช้ในการทำปฏิกิริยาตั้งแต่ 110 ถึง 170 องศาเซลเซียส, เวลาในการทำปฏิกิริยาตั้งแต่ 1 ถึง 8 ชั่วโมง, และอัตราส่วนโดยโมลของคาร์บอนไดออกไซด์ต่อเอทานอลที่ 1:1, 2:1, และ 4:1 ตัวเร่งปฏิกิริยาถูกเตรียมด้วยวิธีการตกตะกอนแบบร่วมที่ร้อยละของซีเรียที่ 0, 7, 20, และ 40 ตามด้วยการเผาที่อุณหภูมิ 500 หรือ 700 องศาเซลเซียส ตัวเร่งปฏิกิริยาถูกวิเคราะห์หาลักษณะเฉพาะด้วยวิธีการ TG-DTA, XRD, BET, และ TPD ผลของการศึกษาพบว่า $\text{Ce}_{0.07}\text{Zr}_{0.93}\text{O}_2$ ที่ได้รับการเผาที่ 700 องศาเซลเซียส ณ ปฏิบัติการที่อัตราส่วนโดยโมลของคาร์บอนไดออกไซด์ต่อเอทานอลที่ 1:1, และอุณหภูมิในการทำปฏิกิริยาที่ 140 องศาเซลเซียส ในระยะเวลาการทำปฏิกิริยา 8 ชั่วโมง ให้ผลการทดสอบตัวเร่งปฏิกิริยาที่สามารถสังเคราะห์ไดเอทิลคาร์บอเนตที่มีค่าการเลือกมากที่สุดที่ร้อยละ 97.5 การปรากฏของเตตระกอนอลเฟสและคุณสมบัติความเป็นกรดต่างที่อ่อนในตัวเร่งปฏิกิริยาดังกล่าวสำคัญต่อการสังเคราะห์ไดเอทิลคาร์บอเนต จากการเปรียบเทียบระหว่างสภาวะเหนือวิกฤตและสภาวะก๊าซในการสังเคราะห์ พบว่าการปฏิบัติการในสภาวะเหนือวิกฤตสามารถเพิ่มปริมาณไดเอทิลคาร์บอเนตที่ถูกสังเคราะห์ขึ้นได้

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