

**CATALYTIC DEHYDRATION OF BIO-ETHANOL TO HYDROCARBONS
OVER SnO_x- AND Sb₂O_x- DOPED ON SAPO-34**

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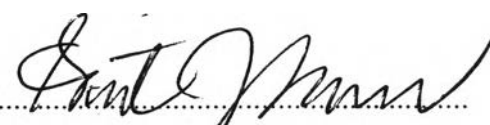
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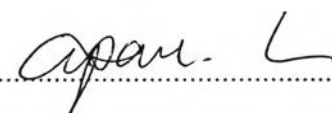
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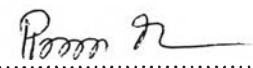
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ABSTRACT

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Recently, bio-ethanol used as a feedstock for catalytic dehydration to obtain aromatic compounds or light hydrocarbons received much attention. SAPO-34 has been employed as a solid acid catalyst for ethanol conversion to light olefins. The introduction of a metal oxide strongly influences on catalytic behavior. Tin oxide and antimony oxide were found to increase the acid strength of SAPO-34, which also increases with the amount of oxygen substitution on the central atom. The aim of this project was to study the impacts of oxidation state of tin and antimony oxides changed with various loading percentages and calcination temperature on bio-ethanol dehydration product. The sole metal oxides were also tested in order to observe its influence for basis in composition. It was found that Sn and Sb metals have hydrogenation properties, resulting in high selectivity of cooking gas. SnO₂ enhanced oligomerization and aromatization reactions of light olefins to bigger hydrocarbons, whereas SnO promotes oxygenate compounds due to its low acidity. For antimony oxide, the selectivity of propylene, cooking gas and butylenes from using Sb₂O₅ was higher than those from Sb₂O₃. On SAPO-34, tin oxide (Sn⁺⁴) was found to enhance propylene, cooking gas, and oxygenates, whereas tin oxide with oxidation 0 was found to promote aromatization to form benzene and C₁₀+ aromatics. The oxidation state of tin oxide +2 was found to enhance oxygenates due to the basic property. Antimony oxide with oxidation state +5 was found to enhance the selectivity of propylene and cooking gas due strong acid strength. Moreover, the increase of calcination temperature was found to promote the agglomeration of Sb₂O₃. Sb₂O₃ on SAPO-34, therefore, behaves like sole antimony oxide. At calcination temperature 700 C°, Sb₂O₃ (Sb⁺³) was observed to promote oxygenate formation, while Sb₂O₅ (Sb⁺⁵) enhanced the formation of non-aromatics and benzene.

บทคัดย่อ

อุรุยา ชินนิยมพานิชย์ : ปฏิริยาดีไฮเดรชันของเอทานอลชีวภาพโดยใช้ตัวเร่งปฏิริยาออกไซด์ของทิน หรือ แอนติโมนีบนซาโปสามสิบสี่ (Catalytic Dehydration of Bio-Ethanol to Hydrocarbons over SnO_x and SbO_x doped SAPO-34) อาจารย์ที่ปรึกษา: รศ. ดร. ศิริรัตน์ จิตการคำ 105 หน้า

ในช่วงที่ผ่านมาเอทานอลชีวภาพสำหรับใช้เป็นสารตั้งต้นสำหรับปฏิริยาดีไฮเดรชันเพื่อผลิตสารอะโรมาติกส์หรือสารไฮโดรคาร์บอน เช่น เอทิลีน โพรพิลีนและพาราไซลีนได้รับความสนใจอย่างแพร่หลาย ซาโปสามสิบสี่เป็นตัวเร่งปฏิริยาที่มีความเป็นกรดซึ่งใช้สำหรับการเปลี่ยนเอทานอลชีวภาพให้เป็นโอเลฟินส์เบา การบรรจุออกไซด์ลงไปบนตัวเร่งปฏิริยามีอิทธิพลต่อพฤติกรรมของตัวเร่งปฏิริยาเป็นอย่างยิ่ง การบรรจุแอนติโมนีออกไซด์และทินออกไซด์บนซาโปสามสิบสี่มีผลทำให้ตัวเร่งปฏิริยามีความแรงของกรดเพิ่มขึ้น และความเป็นกรดนั้นเพิ่มขึ้นตามจำนวนออกซิเจนที่อยู่ติดกับไอออนของโลหะ เป้าหมายของงานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาอิทธิพลของเลขออกซิเดชันของดีบุกและพลวงออกไซด์ที่เปลี่ยนไปตามปริมาณออกไซด์และอุณหภูมิในการเผาที่มีผลต่อผลิตภัณฑ์ที่ได้จากปฏิริยาดีไฮเดรชันของเอทานอลชีวภาพ โดยได้มีการศึกษาอิทธิพลของออกไซด์บริสุทธิ์ของธาตุทั้งสองเพื่อใช้เป็นฐานในการเปรียบเทียบกัน จากการศึกษาพบว่า ทินและแอนติโมนีมีคุณสมบัติในการไฮโดรจิเนชันจึงทำให้ปริมาณก๊าซหุงต้มสูงขึ้น ทินออกไซด์ที่มีเลขออกซิเดชันสี่ส่งเสริมปฏิริยาโอลิโกเมอไรเซชันและอะโรมาไทเซชันของโอเลฟิน ส่วนทินออกไซด์ที่มีเลขออกซิเดชันสองส่งเสริมการเกิดของสารประกอบออกซิเจนเนื่องจากความเป็นกรดต่ำ ส่วนในกรณีของแอนติโมนีออกไซด์นั้น การเกิดของโพรพิลีน ก๊าซหุงต้ม และบิวทิลีนจากการใช้แอนติโมนีออกไซด์ที่มีเลขออกซิเดชันห้า สูงกว่าการใช้ตัวที่มีเลขออกซิเดชันสามเป็นตัวเร่งปฏิริยา แต่เมื่อมีการบรรจุลงไปบนซาโปสามสิบสี่ ทินออกไซด์ที่มีเลขออกซิเดชันสี่ช่วยเพิ่มการเกิดโพรพิลีน ก๊าซหุงต้ม สารประกอบที่มีออกซิเจน ดีบุกออกไซด์ที่มีเลขออกซิเดชันสองนั้น พบว่าส่งเสริมการเกิดสารประกอบออกซิเจนเนื่องตัวมันจากความเป็นเบส ดีบุกออกไซด์ที่มีเลขออกซิเดชันห้าช่วยในการเกิดโพรพิลีนและก๊าซหุงต้มเนื่องจากมีความแข็งแรงของความเป็นกรดสูง นอกจากนี้อุณหภูมิในการเผายังช่วยให้เกิดหลอมรวมของแอนติโมนีไดรอกไซด์ ทำให้มันมีพฤติกรรมเหมือนแอนติโมนีไดรอกไซด์บริสุทธิ์ อีกทั้งเมื่อเพิ่มอุณหภูมิในการเผา แอนติโมนีไดรอกไซด์ช่วยเพิ่มการเกิดสารประกอบที่มีออกซิเจน ส่วนแอนติโมนีเพนตะออกไซด์ส่งเสริมในการเกิดอะโรมาติกและเบนซีน

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