

**PRODUCTION OF SINGLE-WALLED CARBON NANOTUBES BY
DECOMPOSITION OF CARBON-CONTAINING GASES OVER
HETEROGENEOUS CATALYSTS AND THEIR PURIFICATION BY USING
FROTH FLOTATION**

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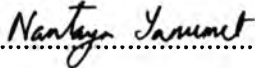
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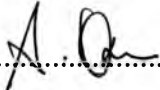
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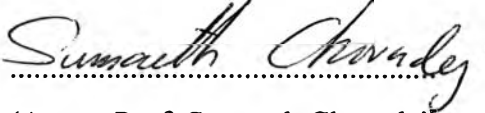
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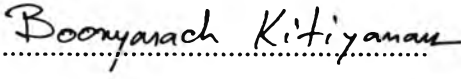

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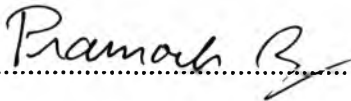
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ABSTRACT

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Pisan Chungchamroenkit: Production of Single-Walled Carbon Nanotubes by Decomposition of Carbon-Containing Gases over Heterogeneous Catalysts and Their Purification by Using Froth Flotation

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In this study, the effects of catalyst formulation, carbon-containing gases, type of catalyst metals, and type of catalyst supports on the synthesis of single-walled carbon nanotube (SWNT) were investigated. It was found that disproportionation of carbon monoxide (CO) over Co-Mo(1:2)/SiO₂ provides a maximum selectivity towards SWNTs. However, when using the Co-Re/SiO₂ catalysts with CO gas, the maximum of both yield and selectivity toward SWNTs were obtained on a Co:Re ratio of 1:4, a pre-reduction temperature of 800°C, and a reaction temperature of 850°C. Furthermore, the catalyst characterization suggests different growth mechanisms of SWNTs on the Co-Re/SiO₂ catalyst from the Co-Mo/SiO₂ catalyst.

To study the purification of the as-prepared SWNTs, carbon black was first used as a representative of SWNTs and tested for separation from SiO₂ by using froth flotation. The maximum carbon black recovery of 70% with an enrichment ratio of 3.5 was achieved with an initial surfactant concentration of 75% of the critical micelle concentration (CMC), a feed solid concentration of 0.02 %w/v, an air flow rate of 200 mL/min, an initial foam height of 50 cm, and no use of an electrolyte. Subsequently, the as-prepared SWNTs were experimentally purified by the NaOH leaching and then froth flotation. From the results, the maximum carbon content of 78%, with a 71% selectivity of SWNTs, was achieved at a surfactant concentration of 75% of the CMC, a solid loading of 1.0 mg/mL, an air flow rate of

100 mL/min, and a foam height of 22 cm. Furthermore, based on pre- and post-treatment characterization, the physical structures of SWNTs were retained after these purification steps.

บทคัดย่อ

พิศาล จึงจำเริญกิจ : การสังเคราะห์คาร์บอนนาโนทิวป์แบบผนังเดี่ยวโดยวิธีการสลายตัวของแก๊สที่มีคาร์บอนเป็นองค์ประกอบบนตัวเร่งปฏิกิริยา และการทำให้บริสุทธิ์โดยใช้กระบวนการทำให้ลอย (Production of Single-Walled Carbon Nanotubes by Decomposition of Carbon-Containing Gases over Heterogeneous Catalysts and Their Purification by Using Froth Flotation) อ. ที่ปรึกษา: รศ. ดร. สุเมธ ชวเวช ผศ. ดร. บุนยรัชต์ กิตติยานันท์ และ ศ. ดร. แคนเน็ล ริชาสโก 142 หน้า

งานวิจัยนี้ได้ทำการศึกษาผลของชนิดของตัวเร่งปฏิกิริยา ชนิดของก๊าซที่มีคาร์บอนเป็นองค์ประกอบ ชนิดของโลหะในตัวเร่งปฏิกิริยา และชนิดของวัสดุที่ใช้เป็นตัวรองรับตัวเร่งปฏิกิริยา ต่อการสังเคราะห์คาร์บอนนาโนทิวป์แบบผนังเดี่ยวพบว่า กระบวนการสลายตัวของก๊าซคาร์บอนมอนอกไซด์บนตัวเร่งปฏิกิริยาโคบอลต์-โมลิบดีนัม ที่มีอัตราส่วนโดยโมล 1 ต่อ 2 บนตัวรองรับซิลิกา (Co-Mo(1:2)/SiO₂) ให้ผลิตภัณฑ์ที่มีสัดส่วนของคาร์บอนนาโนทิวป์แบบผนังเดี่ยวสูงสุด อย่างไรก็ตามเมื่อทดลองใช้การสลายตัวของก๊าซคาร์บอนมอนอกไซด์บนตัวเร่งปฏิกิริยาโคบอลต์-รีเนียมบนตัวรองรับซิลิกา (Co-Re/SiO₂) พบว่าผลิตภัณฑ์ที่ได้มีปริมาณคาร์บอนและสัดส่วนของคาร์บอนนาโนทิวป์แบบผนังเดี่ยวสูงสุด เมื่อใช้อัตราส่วนโดยโมลของโคบอลต์ต่อรีเนียมเป็น 1 ต่อ 4 อุณหภูมิในการรีดิวซ์ที่ 800 องศาเซลเซียส อุณหภูมิในการทำปฏิกิริยาที่ 850 องศาเซลเซียส นอกจากนี้ จากการวิเคราะห์คุณสมบัติของตัวเร่งปฏิกิริยา บ่งชี้ว่า กระบวนการเกิดของคาร์บอนนาโนทิวป์แบบผนังเดี่ยวจากการใช้ตัวเร่งปฏิกิริยาโคบอลต์-รีเนียมบนตัวรองรับซิลิกานั้น ต่างจากการใช้ตัวเร่งปฏิกิริยาโคบอลต์-โมลิบดีนัมบนตัวรองรับซิลิกา

สำหรับการศึกษาการทำให้ผลิตภัณฑ์ที่สังเคราะห์มีความบริสุทธิ์สูงขึ้น โดยใช้กระบวนการทำให้ลอย (Froth flotation) นั้น ได้เริ่มต้นโดยทำการแยกอนุภาคคาร์บอนแบล็คที่ผสมกับอนุภาคซิลิกา กระบวนการนี้สามารถนำอนุภาคคาร์บอนแบล็คกลับคืนมาได้ถึงร้อยละ 70 รวมถึงสัดส่วนคาร์บอนแบล็คต่อซิลิกาที่ได้เท่ากับ 3.5 เท่าของสัดส่วนคาร์บอนแบล็คต่อซิลิกาเริ่มต้น เมื่อใช้ความเข้มข้นเริ่มต้นของสารลดแรงตึงผิวร้อยละ 75 ของความเข้มข้นวิกฤต (CMC) ปริมาณของแข็งในสารละลายเริ่มต้นร้อยละ 0.02 โดยมวลต่อปริมาตร อัตราการไหลของอากาศ 200 มิลลิลิตรต่อนาที ความสูงเริ่มต้นของชั้นฟอง 50 เซนติเมตร และไม่เติมอิเล็กโทรไลต์ จากนั้นได้ทำการทดลองการทำให้คาร์บอนนาโนทิวป์แบบผนังเดี่ยวที่สังเคราะห์ได้มีความบริสุทธิ์สูงขึ้น โดยใช้การชะด้วยโซเดียมไฮดรอกไซด์ร่วมกับกระบวนการทำให้ลอย จากผลการทดลองพบว่า ปริมาณคาร์บอนในผลิตภัณฑ์ที่ทำให้บริสุทธิ์สูงถึงร้อยละ 78 และสัดส่วนของคาร์บอนนาโนทิวป์

แบบผนังเดี่ยวร้อยละ 71 ได้จากการใช้ความเข้มข้นเริ่มต้นของสารลดแรงตึงผิวร้อยละ 75 ของความเข้มข้นวิกฤต ปริมาณของอนุภาค 1.0 มิลลิกรัมต่อมิลลิลิตร อัตราการไหลของอากาศ 100 มิลลิลิตรต่อนาที ความสูงเริ่มต้นของชั้นฟอง 22 เซนติเมตร จากการวิเคราะห์สมบัติทั้งก่อนและหลังจากกระบวนการทำให้บริสุทธิ์ พบว่ากระบวนการนี้ไม่ทำให้โครงสร้างของคาร์บอนนาโนทิวป์แบบผนังเดี่ยวได้รับความเสียหาย

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