



รายงานวิจัยฉบับสมบูรณ์

โครงการ

สถาบันวิจัยเกี่ยวกับตัวเร่งปฏิกิริยาไทย

Thai Catalysis Research Institute

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และสำนักงานกองทุนสนับสนุนการวิจัย

(ความเห็นในรายงานนี้เป็นของผู้วิจัย สกอ.และสกว. ไม่จำเป็นต้องเห็นด้วยเสมอไป)

บทคัดย่อ

โครงการวิจัยนี้ได้ศึกษาตัวเร่งปฏิกิริยาหลากหลายชนิดสำหรับปฏิกิริยาต่าง ๆ กัน โดยทั่วไปได้ทำการสังเคราะห์ตัวเร่งปฏิกิริยาขึ้นมา ทดสอบคุณลักษณะต่างของตัวเร่งปฏิกิริยาดังกล่าว แล้วนำไปใช้ในปฏิกิริยาที่เหมาะสม ซึ่งจะเห็นว่าการประยุกต์ใช้ตัวเร่งปฏิกิริยาเหล่านี้มากมายในงานวิจัยดังกล่าวนี้ ได้แก่ ปฏิกิริยาการจัดนำของเมทานอล การเร่งปฏิกิริยาโดยแสง ออกซิเดชันของโพรเพนและการบอมนอกไซด์ เอสเทอริฟิเคชันและทรานส์เอสเทอริฟิเคชัน พอลิเมอร์ไรเซชันของเอทิลีนโดยตัวเร่งปฏิกิริยาซีเกลอร์-นัตตาและเมทัลโลซีน การผลิตไฮโดรเจนสำหรับเซลล์เชื้อเพลิง ปฏิกิริยาไอโซเมอร์ไรเซชันของบิวเทน ไฮโดรจิเนชันของการบอมนอกไซด์ และปฏิกิริยาเมตาทีซิส ผลการวิจัยดังกล่าวทำให้สามารถผลิตบทความวิจัยที่ได้รับการตีพิมพ์ในระดับนานาชาติจำนวน 32 เรื่อง และสิทธิบัตรจำนวน 1 เรื่อง

คำสำคัญ ตัวเร่งปฏิกิริยาแบบวิวิธพันธุ์; ความว่องไว; ภูมิภาคแก๊ส; ภูมิภาคของเหลว; การทดสอบคุณลักษณะ

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Abstract

In this present study, we investigated many kinds of catalysts used in various reactions. In general, the catalysts were synthesized, characterized and tested under specified reaction conditions. There are many applications of catalyst used in this project such as methanol dehydration, photocatalysis, propane oxidation, CO oxidation, esterification and transesterification, ethylene polymerization catalysts (Ziegler-Natta and metallocene catalysts), hydrogen production for fuel cell application, isomerization of butane, CO hydrogenation, and metathesis reaction. As the results, we can produce 32 international research articles (JCR database) and 1 patent.

Keywords: Heterogeneous catalyst; Activity; Gas phase; Liquid phase; Characterization

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Executive Summary

1. ความสำคัญและที่มาของปัญหา

จากการสำรวจกำลังคนเพื่อสนองตอบต่ออุตสาหกรรมน้ำมันและปิโตรเคมีของประเทศ ซึ่งจัดทำโดยสำนักงานคณะกรรมการพัฒนาเศรษฐกิจและสังคมแห่งชาติพบว่า ศาสตร์เกี่ยวข้องกับตัวเร่งปฏิกิริยาเป็นองค์ความรู้หนึ่งที่อุตสาหกรรมน้ำมันและปิโตรเคมีของประเทศต้องการความช่วยเหลือจากรัฐ ในปัจจุบัน เฉพาะนิคมอุตสาหกรรมมาบตาพุด อำเภอเมือง จังหวัดระยอง มีโรงงานอุตสาหกรรมปิโตรเคมีและอุตสาหกรรมที่เกี่ยวข้องอยู่กว่า 40 โรงงาน เป็นเงินลงทุนทั้งสิ้นกว่า 1.3 ล้านล้านบาท (<http://www.boi.go.th>) สามารถส่งออกสินค้าสู่ตลาดต่างประเทศมากกว่าร้อยละ 40 ของการผลิตทั้งหมด นำเงินรายได้เข้าสู่ประเทศเป็นจำนวนมหาศาล ดังนั้นรัฐน่าจะลงทุนสร้างสถาบันวิจัยเฉพาะทางเพื่อสนับสนุนอุตสาหกรรมน้ำมันและปิโตรเคมีในประเทศ งานวิจัยหนึ่งที่สำคัญที่เกี่ยวข้องกับอุตสาหกรรมเหล่านี้ได้แก่ การวิจัยทางด้านตัวเร่งปฏิกิริยา

จากรายงานการศึกษาเพื่อจัดทำยุทธศาสตร์การพัฒนาทรัพยากรมนุษย์เพื่อเพิ่มขีดความสามารถของอุตสาหกรรม โดยสำนักงานคณะกรรมการพัฒนาการเศรษฐกิจและสังคมแห่งชาติ ที่นำเสนอเมื่อวันที่ 9 พฤษภาคม 2547 ได้ประมาณการไว้ว่าในส่วนของการผลิตพอลิเมอร์หลัก (Polyethylene, Polypropylene, Polyvinyl chloride, Polystyrene/EPS, ABS/SAN) มีทิศทางและแนวโน้มที่จะเพิ่มกำลังการผลิตขึ้น โดยความต้องการรวมของปีพ.ศ. 2547 มีประมาณการที่ 3,757,000 ตัน และจะเพิ่มเป็น 5,265,000 ตัน (เพิ่มอีกประมาณร้อยละ 40) ในปีพ.ศ. 2552 และจากการสำรวจความต้องการบุคลากรในบริษัทขนาดใหญ่จำนวน 13 บริษัทพบว่า ในด้านการวิจัยและพัฒนาผลิตภัณฑ์ (Product Research & Development) นั้น ปัญหาความขาดแคลนบุคลากรทางด้านการพัฒนาตัวเร่งปฏิกิริยา (Catalyst development) อยู่ในอันดับต้น โดยความต้องการที่แท้จริงอยู่ที่ประมาณ 1 เท่าตัวของที่มีอยู่ในปัจจุบัน โดยเฉพาะอย่างยิ่งการขาดแคลนอาจารย์ที่เชี่ยวชาญเฉพาะด้าน เช่นด้านตัวเร่งปฏิกิริยา ทำให้เป็นปัญหาในการผลิตบุคลากรที่มีความรู้ความสามารถทางด้านนี้ โดยความต้องการบุคลากรด้านวิทยาศาสตร์และเทคโนโลยีในปีพ.ศ. 2547 มีการประมาณการไว้ที่ 5,383 คน และในอีก 2 ปีข้างหน้า (พ.ศ. 2549) จะเพิ่มเป็น 6,280 คน (เพิ่มอีกประมาณร้อยละ 17)

จากการประชุมเพื่อระดมความคิดเพื่อสร้างงานวิจัยร่วมระหว่างศูนย์เชี่ยวชาญด้านคatalาไลซิสและวิศวกรรมตัวเร่งปฏิกิริยาที่ใช้ตัวเร่งปฏิกิริยาและหน่วยงานภาคเอกชนที่จัดโดยสำนักงานกองทุนสนับสนุนการวิจัย (สกว.) ณ สำนักงานกองทุนสนับสนุนการวิจัย เมื่อวันที่ 4 สิงหาคม 2547 โดยมีผู้แทนจากภาคอุตสาหกรรมเข้าร่วมแสดงความคิดเห็นจาก 5 หน่วยงานดังนี้

1. สถาบันวิจัย บริษัท การปิโตรเลียมแห่งประเทศไทย จำกัด (มหาชน)
2. บริษัท ปิโตรเคมีแห่งชาติ จำกัด (มหาชน)
3. บริษัท คอนทีเนนทอลปิโตรเคมีคอล (ประเทศไทย) จำกัด
4. บริษัท ไทยโอเลฟินส์ จำกัด
5. บริษัท ระยองโอเลฟินส์ จำกัด

ผลจากการประชุมดังกล่าวได้ข้อสังเกต 2 ข้อดังนี้

ข้อสังเกตข้อที่ 1 : การจับกลุ่มบริษัทที่สนใจในตัวเร่งปฏิกิริยาที่ใกล้เคียงกัน

ในปัจจุบันการใช้ตัวเร่งปฏิกิริยาในประเทศไทยสามารถแบ่งออกได้เป็น 2 ส่วนหลักคือ ก) โรงกลั่นน้ำมัน และ ข) อุตสาหกรรมเคมีและปิโตรเคมี

โดยโรงกลั่นน้ำมันเป็นกลุ่มแรกที่มีการใช้ตัวเร่งปฏิกิริยาบางชนิดในปริมาณมากเพราะโรงกลั่นน้ำมันจะมีกำลังการผลิตที่สูง (ระดับ 1 ล้านบาร์เรลต่อวันขึ้นไป) จำนวนโรงกลั่นมีอยู่ไม่มากนักลักษณะของโรงกลั่นน้ำมันจะเป็นบริษัทข้ามชาติที่มีบริษัทแม่อยู่ต่างประเทศ เทคโนโลยีการผลิตต่าง ๆ รวมทั้งการแก้ปัญหาต่าง ๆ ที่เกิดขึ้นส่งตรงมาจากต่างประเทศ ในขณะที่กลุ่มอุตสาหกรรมเคมีและปิโตรเคมีนั้นบริษัทส่วนใหญ่จะมีฝ่ายไทยเป็นผู้ถือหุ้นรายใหญ่ในบริษัท โดยซื้อเทคโนโลยีจากต่างประเทศ บริษัทในกลุ่มอุตสาหกรรมเคมีและปิโตรเคมีมีการใช้ตัวเร่งปฏิกิริยาหลากหลายประเภทมากกว่าที่ใช้กันในโรงกลั่นน้ำมัน จำนวนบริษัท/โรงงานต่าง ๆ ที่อยู่ในส่วนอุตสาหกรรมเคมีและปิโตรเคมีมีมากกว่าส่วนโรงกลั่นน้ำมัน การจับคู่บริษัทที่มีความสนใจตัวเร่งปฏิกิริยาที่คล้ายคลึงกันและ/หรือมีแนวทางการทำวิจัยในหัวข้อที่ใกล้เคียงกันจึงทำได้ยาก

ข้อสังเกตข้อที่ 2 : การจัดตั้งหน่วยงานเพื่อแก้ปัญหาตัวเร่งปฏิกิริยาที่บริษัทประสบ

ในปัจจุบัน ปัญหาที่สำคัญของอุตสาหกรรมที่ต้องเกี่ยวข้องกับตัวเร่งปฏิกิริยาคือ

- ก) การเลือกใช้ตัวเร่งปฏิกิริยาให้เหมาะสมกับกระบวนการผลิต
- ข) การใช้ตัวเร่งปฏิกิริยาที่มีอยู่ปัจจุบันได้ผลผลิตที่เป็นไปตามข้อกำหนด
- ค) การยืดอายุการทำงานของตัวเร่งปฏิกิริยา

ซึ่งปัญหาทั้ง 3 รูปแบบจะเน้นไปที่การเลือกใช้และการใช้งานอย่างคุ้มค่า ซึ่งโดยทั่วไปตัวเร่งปฏิกิริยาเมื่อซื้อมาใช้แต่ละครั้งจะมีอายุการทำงานหลายปี ถ้าหากทางบริษัทลงทุนจัดตั้งหน่วยงานเพื่อทำวิจัยเพื่อแก้ปัญหาที่ทางบริษัทประสบ และเมื่อแก้ปัญหาได้แล้วหน่วยงานที่จัดตั้งขึ้นมาใหม่นั้นจะเกิดการขาดช่วงการทำงาน ทำให้ทางบริษัทเองพึงพอใจที่จะจ้างหน่วยงานวิจัยภายนอกให้ทำวิจัยแทนมากกว่า แต่จำนวนหน่วยงานภายนอกที่สามารถทำวิจัยแทนได้ก็มีจำนวนจำกัดมาก (หน่วยงานหนึ่งที่เป็นที่ยอมรับคือศูนย์เชี่ยวชาญด้านคาตาไลซิสและวิศวกรรมปฏิกิริยาที่ใช้ตัวเร่งปฏิกิริยา ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย) สถานการณ์ในปัจจุบันเองมีเพียงบางบริษัทเท่านั้นที่ได้เริ่มทำการศึกษาพัฒนาตัวเร่งปฏิกิริยาเพื่อใช้งานเองโดยมีวัตถุประสงค์หลักเพื่อลดค่าใช้จ่ายซื้อตัวเร่งปฏิกิริยาจากต่างประเทศ บริษัทเหล่านี้เป็น

บริษัทที่อยู่ในกลุ่มผลิตเม็ดพลาสติก (เช่น HDPE, LLDPE, PP) เพราะลักษณะกระบวนการผลิตพลาสติกในในกลุ่มนี้จะต้องสูญเสียตัวเร่งปฏิกิริยาโดยการผสมเข้าไปกับผลิตภัณฑ์เม็ดพลาสติกที่ผลิตได้ตลอดเวลา จึงจำเป็นต้องมีการนำเข้าตัวเร่งปฏิกิริยาอย่างต่อเนื่อง นอกจากนี้สมบัติพลาสติกที่ได้ยังขึ้นอยู่กับตัวเร่งปฏิกิริยาที่ใช้ ทำให้เกิดความคุ้มค่าที่จะตั้งหน่วยงานเพื่อทำการวิจัยและผลิตตัวเร่งปฏิกิริยาที่ได้จากการวิจัยเพื่อนำมาใช้งานเองในบริษัท เพราะจะทำให้สามารถผลิตพลาสติกได้หลากหลายชนิดมากขึ้น และยังไม่ต้องกังวลว่าจะถูกจำกัดกำลังการผลิตด้วยการจำกัดปริมาณตัวเร่งปฏิกิริยาที่เจ้าของเทคโนโลยีจะขายให้

ตัวเร่งปฏิกิริยามีวิวัฒนาการที่มีการใช้งานกันอยู่ในปัจจุบันสามารถแบ่งได้เป็น 3 ประเภท คือ 1) ตัวเร่งปฏิกิริยาที่ทำจากโลหะ 2) ตัวเร่งปฏิกิริยาที่ทำจากโลหะออกไซด์ และ 3) ตัวเร่งปฏิกิริยาในตระกูลซีโอไลต์ โดยที่ตัวเร่งปฏิกิริยาแต่ละประเภทจะมีลักษณะเฉพาะของมันเอง ซึ่งต้องการการศึกษาที่จะลึกในทุกด้านซึ่งรวมถึง ความว่องไวในการทำปฏิกิริยาที่ต้องการ การเลือกเกิดเฉพาะผลิตภัณฑ์ที่ต้องการ อายุการใช้งาน และการเสื่อมสภาพของตัวเร่งปฏิกิริยา

จากสถิติของกรมศุลกากรในปีพ.ศ. 2544-2547 (ตารางที่ 1) จะเห็นว่าประเทศไทยนำเข้าตัวเร่งปฏิกิริยาจากประเทศต่าง ๆ เป็นมูลค่าประมาณ 3,000 ล้านบาทในแต่ละปี แต่ราคาตัวเร่งปฏิกิริยายังไม่ใช่เป็นราคาส่วนใหญ่ของการผลิตสินค้า เพราะถ้าการทำงานของตัวเร่งปฏิกิริยาไม่เป็นไปตามต้องการจะทำให้ไม่สามารถผลิตสินค้าได้ตามมาตรฐานที่กำหนด ทำให้ผู้ผลิตสูญเสียโอกาส และสูญเสียวัสดุที่ใช้ในการผลิต ซึ่งเมื่อคิดเป็นมูลค่าแล้วจะพบว่าสูงกว่าราคาตัวเร่งปฏิกิริยาหลายเท่าตัว

ตารางที่ 1 มูลค่าการนำเข้าตัวเร่งปฏิกิริยาของประเทศไทยในช่วงปีพ.ศ. 2544-2547 (ที่มา: เว็บไซต์ของกรมศุลกากร <http://www.customs.go.th> โดยตัวเร่งปฏิกิริยาอยู่ในกลุ่มรหัส HS code 3815)

ปีพ.ศ.	มูลค่าการนำเข้า CIF (บาท)
2545	2,755,654,105
2546	3,626,037,254
2547 (มกราคม - สิงหาคม)	2,312,783,834

ศูนย์เชี่ยวชาญเฉพาะทางด้านคาตาไลซิสและวิศวกรรมปฏิกิริยาที่ใช้ตัวเร่งปฏิกิริยา (Centre of excellence on catalysis and catalytic reaction engineering - ต่อไปจะเรียกอย่างสั้นว่า "ศูนย์เชี่ยวชาญฯ") ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย มีประสบการณ์ทำงานวิจัยทางด้านตัวเร่งปฏิกิริยามานานกว่า 20 ปี ปัจจุบันมีคณาจารย์ 9 ท่าน และนิสิตระดับปริญญาเอกและปริญญาโทที่ทำวิจัยอยู่จำนวนเฉลี่ยไม่ต่ำกว่า 60 คนต่อปี มีอุปกรณ์วิจัยที่ทันสมัย

และสามารถผลิตผลงาน ตีพิมพ์ในวารสารนานาชาติได้อย่างต่อเนื่อง โดยงานวิจัยที่ได้รับการตีพิมพ์มีจุดเด่นหลักคือเป็นงานที่ผลิตขึ้นเองในห้องปฏิบัติการของศูนย์เชี่ยวชาญฯ โดยไม่จำเป็นต้องพึ่งพาห้องปฏิบัติการหรือบุคลากรจากต่างประเทศ

ศูนย์เชี่ยวชาญฯ มีศักยภาพในการเป็นศูนย์กลาง (Hub) ทางด้านตัวเร่งปฏิกิริยา เพราะมีความร่วมมือกับบุคลากรของมหาวิทยาลัยต่าง ๆ ในประเทศอย่างต่อเนื่อง อาทิเช่น มหาวิทยาลัยสงขลานครินทร์ มหาวิทยาลัยศิลปากร และ สถาบันเทคโนโลยีพระจอมเกล้า วิทยาเขตเจ้าคุณทหาร ลาดกระบัง เป็นต้น และยังมีความร่วมมือด้านการแลกเปลี่ยนนักวิจัยกับมหาวิทยาลัยชั้นนำหลายแห่งในโลก อาทิเช่น University of Waterloo, University of Alberta ประเทศแคนาดา Tokyo Institute of Technology, Kyoto University, Nakoya University, Japan Advanced Institute of Science and Technology ประเทศญี่ปุ่น University of New South Wales ประเทศออสเตรเลีย เป็นต้น

อนึ่งศูนย์เชี่ยวชาญฯ ยังมีประสพการณ์ในการทำวิจัยร่วมกับบริษัทต่างๆ เช่น สถาบันวิจัยของบริษัท การปิโตรเลียมแห่งประเทศไทย จำกัด (มหาชน) บริษัท คอนทิเนนทอล ปิโตรเคมีคอล (ประเทศไทย) จำกัด บริษัท บางกอกโพลีเอทิลีน จำกัด (มหาชน) และบริษัท ระยองโอเลฟิน จำกัด เป็นต้น นอกจากนี้ในปี พ.ศ. 2547 ศูนย์เชี่ยวชาญฯ จะได้รับครุภัณฑ์จากโครงการเงินกู้จากธนาคาร JBIC ประเทศญี่ปุ่น ในวงเงินประมาณ 50 ล้านบาท โครงการวิจัยร่วมกับ บริษัท Mektec Manufacturing Cooperation (Thailand) จำกัด ในโครงการ Research and Development of Flexible Printed Circuit using Nanotechnology ในวงเงินมากกว่า 200 ล้านบาท โครงการร่วมมือวิจัยเกี่ยวกับตัวเร่งปฏิกิริยากับ PTT Research and Technology Institute, PTT Chemical Public Company Limited, Siam Cement Group and UBE Group (Thailand) ในวงเงินประมาณ 100 ล้านบาท

2. วัตถุประสงค์

เพื่อเป็นศูนย์กลางสนับสนุนการวิจัยพัฒนาและการใช้ตัวเร่งปฏิกิริยาของอุตสาหกรรมปิโตรเลียม อุตสาหกรรมปิโตรเคมี และตัวเร่งปฏิกิริยาที่ใช้ในการกำจัดมลพิษในประเทศ

3. ระเบียบวิธีวิจัยโดยสรุป

การวิจัยที่เกี่ยวข้องกับตัวเร่งปฏิกิริยาจะแบ่งออกเป็น 3 ส่วนคือ

- 1) วิธีการเตรียมตัวเร่งปฏิกิริยา
- 2) วิธีการทดสอบตัวเร่งปฏิกิริยา
- 3) วิธีการวัดคุณลักษณะของตัวเร่งปฏิกิริยาหรือผลิตภัณฑ์ที่เกิดขึ้น

โดยตัวเร่งปฏิกิริยาแต่ละประเภทจะมีวิธีการวิจัยที่แตกต่างกัน จึงจำเป็นต้องแยกวิธีวิจัยของตัวเร่งปฏิกิริยาประเภทต่าง ๆ ดังตัวอย่างที่ยกมาพอสังเขปดังนี้

3.1 ตัวเร่งปฏิกิริยาเมทัลโลซีนและซิกเกอร์-แนทตา

3.1.1 การเตรียมตัวเร่งปฏิกิริยา Ziegler Natta

1. ใส่ Anhydrous Chloride 0.476 g ลงใน Schlenk tube ขนาด 100 ml
2. ชั่ง Phthalic Anhydride 0.1089 g ลงในขวด
3. นิด Decane 2.5 ml ลงใน schlenk ปั่นกวนและเพิ่มอุณหภูมิช้า ๆ จนถึง 130°C
4. นิด 2-Ethyl-Hexanol 2.34 ml ที่อุณหภูมิ 130°C นาน 2 ชั่วโมง
5. เติม Phthalic Anhydride ที่อุณหภูมิ 130°C นาน 1 ชั่วโมง
6. ปิด heater และ stirrer ทิ้งไว้ 1 คืน
7. ปรับอุณหภูมิให้ได้ -20°C
8. ปั่นกวนช้า ๆ แล้วค่อย ๆ หยด TiCl_4 20 ml ที่ -20°C นาน 1 ชั่วโมง
9. ปลอ่ยให้อุณหภูมิลดลง ๆ สูงขึ้นจนถึงอุณหภูมิห้อง
10. เพิ่มอุณหภูมิช้า ๆ จนถึง 110°C ในเวลา 4 ชั่วโมง
11. หยด Diethyl Phthalate 0.26 ml ที่อุณหภูมิ 110°C นาน 2 ชั่วโมง
12. ทิ้งให้ตกตะกอน (1.5 ชั่วโมง) แล้วดูดของเหลวออก
13. ค่อย ๆ หยด TiCl_4 20 ml ที่อุณหภูมิห้อง
14. เพิ่มอุณหภูมิจนถึง 120°C ในเวลา 4 ชั่วโมง ควบคุมอุณหภูมิที่ 120°C นาน 2 ชั่วโมง
15. ทิ้งให้ตกตะกอนแล้วดูดของเหลวออก
16. ล้างตะกอนด้วย Decane 10 ml 2 รอบ และ Hexane 10 ml 3 รอบ
17. ทำตะกอนให้แห้งโดยใช้ระบบ Vacuum

3.1.2 การเตรียมตัวเร่งปฏิกิริยา metallocene

การเตรียม Catalyst Precursor

1. นำซิลิกาที่ทำการ calcine โดยให้ความร้อนที่ 400°C นาน 6 ชั่วโมง ภายใต้ภาวะสูญญากาศมา 940 mg ใส่ใน schlenk tube ขนาด 100 ml โดยชั่งใน glove box
2. เติม toluene 10 ml ภายใต้ภาวะอาร์กอน
3. เติม MAO 16 mmol ภายใต้ภาวะอาร์กอน
4. กวนให้เข้ากันนาน 30 นาที ที่อุณหภูมิห้อง

5. คูดสารละลายไฮดรอกไซด์และล้างของแข็งด้วย toluene 20 ml 5 ครั้งภายใต้บรรยากาศอาร์กอน
6. ทำให้แห้งในสุญญากาศที่อุณหภูมิห้อง

การเตรียมตัวเร่งปฏิกิริยา metallocene บนตัวรองรับ

1. เติมน้ำมันละลายตัวเร่งปฏิกิริยา metallocene 8 μmol ภายใต้บรรยากาศอาร์กอนลงใน Catalyst precursor ที่อยู่ใน schlenk
2. กวนให้เข้ากันนาน 30 นาทีที่อุณหภูมิห้อง
3. คูดสารละลายไฮดรอกไซด์และล้างของแข็งด้วยโทลูอีน 20 ml 2 ครั้ง ภายใต้บรรยากาศอาร์กอน
4. ทำให้แห้งในสุญญากาศที่อุณหภูมิห้อง

3.1.3 การทดสอบตัวเร่งปฏิกิริยา

นำตัวเร่งปฏิกิริยาไปทำปฏิกิริยา polypropylene polymerization

1. อบ autoclave reactor ขนาด 100 ml และ magnetic bar ให้แห้งที่อุณหภูมิ 110°C เป็นเวลา 30 นาที
2. ใส่ตัวเร่งปฏิกิริยาและตัวเร่งปฏิกิริยาร่วมลงใน reactor ที่อุณหภูมิห้องภายใน glove box แล้วทำการกวนทิ้งไว้ 5 นาที
3. ใส่แก๊สออกจาก reactor แล้วแช่ reactor ลงใน water bath เพื่อควบคุมอุณหภูมิตามอุณหภูมิ polymerization
4. เริ่มปฏิกิริยา polymerization โดยป้อนแก๊ส propylene เข้าสู่ reactor แล้วทิ้งให้เกิดปฏิกิริยาตาม polymerization time
5. หยุดปฏิกิริยาโดยระบายแก๊ส propylene ออก แล้วเติมกรดใน methanol
6. ล้างพอลิเมอร์ที่ได้ด้วยเมทานอลทันที แล้วทำให้แห้งที่อุณหภูมิห้อง
7. นำพอลิเมอร์ไปชั่งแล้วนำไปหาค่าความสามารถในการเร่งปฏิกิริยา (activity)

3.1.4 การวัดสมบัติของตัวเร่งปฏิกิริยาหรือผลิตภัณฑ์ที่ได้

3.1.4.1. Small Angle Light Scattering (SALS)

เครื่อง static light scattering ที่ห้องทดลองโพลิเมอร์ ภาควิชาวิศวกรรมเคมี จุฬาลงกรณ์มหาวิทยาลัย ใช้ He/Ne laser ($\lambda = 632.8 \text{ nm}$) เป็นแหล่งกำเนิดแสง นำตัวอย่างใส่ใน holder ซึ่งตั้งอยู่ระหว่าง polarizer 2 อัน โดยทิศทางการเกิด polarization ของ polarizer ใกล้เคียงกับแหล่งกำเนิด

แสงอยู่ในแนวตั้งส่วนที่เหลืออยู่ในแนวนอน กราฟการกระเจิงของแสงถูกตรวจสอบด้วย CCD Camera ในเวลา 2 นาที ความสว่างของต้นกำเนิดแสงเลเซอร์ตั้งไว้ที่ตำแหน่ง 6 (gain 6) และ 10 (gain 10) โดยใช้คอมพิวเตอร์โปรแกรมซึ่งต่อเข้ากับเครื่องวิเคราะห์ กราฟที่ได้ถูกส่งเข้าวิเคราะห์ด้วยคอมพิวเตอร์

3.1.4.2. Scanning Electron Microscopy (SEM)

เครื่อง scanning electron microscope JSM-5410 ที่ Scientific and Technological Research Equipment Center จุฬาลงกรณ์มหาวิทยาลัย SEM ทำงานที่ 1.5 kV ซึ่งเป็นภาวะที่เหมาะสมเพราะถ้าค่าสูงเกินไปจะทำให้ตัวอย่างไหม้ ในเครื่อง scanning electron microscope ถ้าอิเล็กตรอนจะถูกสแกนผ่านพื้นผิวของตัวอย่างที่บดแสง เมื่อลำอิเล็กตรอนกระทบพื้นผิวของตัวอย่าง ความแตกต่างของความหนาแน่นของอิเล็กตรอนในตัวอย่างจะทำให้เกิดการกระเจิงของอิเล็กตรอน และการแผ่รังสีของอิเล็กตรอนเหล่านี้จะถูกวัด ปรับเปลี่ยน และใช้ลดความสว่างของลำแสงครั้งที่ 2 ใน cathode ray tube (CRT) ในเวลาเดียวกัน จุดที่มีการสะสมมากจะเกิดเป็นจุดสว่างในขณะที่จุดที่มีสัญญาณน้อยจะเป็นจุดที่สว่างน้อยกว่า

เนื่องจากวิธีการนี้ต้องใช้ตัวอย่างที่นำไฟฟ้าได้ดี ดังนั้นจึงต้องเตรียมตัวอย่างให้สภาพการนำโดยเคลือบตัวอย่างด้วยชั้นโลหะบาง ๆ การทดลองนี้ใช้ทองคำมาเคลือบตัวอย่างเป็นฟิล์มบางและเก็บในที่ที่แห้งก่อนทำการทดลอง

3.1.4.3. Thermal Gravimetry Analysis (TGA)

การวิเคราะห์ทำด้วยเครื่อง SDT Q600 ตัวอย่างน้ำหนักประมาณ 10-20 มิลลิกรัมถูกบรรจุในถ้วยอะลูมิเนียมขนาด 90 ไมโครลิตร ตัวอย่างจะถูกให้ความร้อนจนถึงอุณหภูมิ 800°C ด้วยอัตรา 10°C/min โดยใช้ไนโตรเจนไหลผ่าน

3.1.4.4. X-Ray Diffraction (XRD)

เอ็กซ์เรย์ดิฟแฟร็กโตแกรมถูกวัดด้วยเครื่อง SIEMENS D5000 โดยใช้รังสี CuK α (ความยาวคลื่นเท่ากับ 1.54 อังสตรอม) ที่ 30 kV และ 30 mA และมีแผ่นกรองนิกเกิล ความเป็นผลึกของตัวอย่างจะถูกวัดในช่วง $2\theta = 20^\circ$ ถึง $2\theta = 80^\circ$ ที่ความละเอียด 0.04°

3.1.4.5. C-Nuclear Magnetic Resonance (^{13}C -NMR)

เครื่อง ^{13}C -NMR spectroscopy ถูกใช้ในการตรวจสอบโครงสร้างจุลภาคของพอลิเมอร์ ตัวอย่างถูกละลายใน 1,2,4-trichlorobenzene และ dichlorobenzene- d_6 (20 vol%) สำหรับ internal lock ^{13}C -NMR spectra ทำที่ 110°C ด้วยเครื่อง Bruker Avance II 400 ปฏิบัติการที่ 100 MHz โดยใช้เวลารวบรวมข้อมูล 1.5 วินาทีและเวลารวบรวม 4 วินาที

3.1.4.6. Fourier Transformed Infrared Spectroscopy (FT-IR)

เครื่อง Nicolet FT-IR Impact 400 Spectrophotometer ที่ Center of Excellence on Catalysis and catalytic Reaction Engineering ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์

มหาวิทยาลัย เทคนิคการใช้ FT-IR ใช้กันกว้างขวางในการดูลักษณะโครงสร้างของโพลิเมอร์ การบันทึก IR spectrum จะทำการรวบรวม 32 ครั้ง ในช่วง $4000-400\text{ cm}^{-1}$ โดยมีความละเอียด 4 cm^{-1} การเปรียบเทียบตำแหน่งการดูดกลืน IR spectrum ของโพลิเมอร์ตัวอย่าง ลักษณะการดูดกลืนจะสามารถหาค่า band และกลุ่มฟังก์ชันที่มีในโพลิเมอร์ IR spectrum ของโพลิเมอร์จะมีลักษณะเฉพาะที่สามารถพิจารณาได้จาก fingerprint”

3.1.4.7. Differential Scanning Calorimeter (DSC)

การวิเคราะห์ทำด้วยเครื่อง Perkin-Elmer DSC-7 เพื่อหาอุณหภูมิในการหลอมเหลวและความเป็นผลึกของโพลิเมอร์ ตัวอย่างถูกให้ความร้อนจนถึงอุณหภูมิ 200°C ด้วยอัตรา $10^{\circ}\text{C}/\text{min}$ อุณหภูมินี้สูงกว่าอุณหภูมิในการหลอมเหลวของโพลิเมอร์พอลิเมอร์และถูกคงไว้เป็นเวลานาน 10 นาที จากนั้นลดอุณหภูมิลงด้วยอัตรา $10^{\circ}\text{C}/\text{min}$ จนถึงอุณหภูมิ 30°C เพื่อให้เกิดการตกผลึกขึ้น ตัวอย่างจะถูกให้ความร้อนอีกครั้งที่อัตราการเพิ่มอุณหภูมิ $10^{\circ}\text{C}/\text{min}$ ผลการวิเคราะห์จะถูกบันทึกในการให้ความร้อนครั้งที่สองเพื่อกำจัดความทรงจำทางความร้อนของโพลิเมอร์

3.2 ตัวเร่งปฏิกิริยาโลหะออกไซด์

3.2.1 เตรียมตัวเร่งปฏิกิริยาแวนเดียมบนไททาเนีย

1. เตรียมสารแขวนลอยไททาเนียออกไซด์ โดยนำ TiO_2 ปริมาณ 4.65 g มาละลายในน้ำ 50 ml
2. นำสารแขวนลอย TiO_2 มาเพิ่มอุณหภูมิเป็น 70°C
3. เตรียม NH_4VO_3 ปริมาณ 0.45 g และนำมาผสมในสารแขวนลอย TiO_2 ที่ 70°C
4. นำสารแขวนลอยที่ได้ไประเหยน้ำออกที่อุณหภูมิ 80°C นาน 5 ชั่วโมง
5. นำของแข็งที่ได้ไปอบในตู้อบที่อุณหภูมิ 110°C เป็นเวลา 24 ชั่วโมง
6. นำของแข็งที่ผ่านการอบมา Calcine ด้วยอากาศที่มีอัตราการไหล $100\text{ ml}/\text{min}$ ที่ 550°C เป็นเวลา 6 ชั่วโมง จะได้แวนเดียมบนไททาเนีย

3.2.2 การเติมโลหะทรานซิชันลงบนตัวเร่งปฏิกิริยา

1. นำแวนเดียมบนไททาเนีย 5 g มาใส่ในน้ำ 50 ml
2. นำสารแขวนลอยจากข้อ 1. มาเพิ่มอุณหภูมิเป็น 70°C
3. เตรียมเกลือของโลหะที่ต้องการปริมาณตามตารางด้านล่าง และ MgNO_3 ปริมาณ 0.5791 g มาละลายในสารแขวนลอยข้อ 2.

ตารางที่ 2 การเติมโลหะตัวที่สอง

โลหะที่เติม	สารเคมี	ปริมาณ (g)
Mo	Ammonium molybdate ((NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O)	0.8
Cu	Cupric nitrate trihydrate (CuN ₂ O ₆ ·3H ₂ O)	1.6531
Fe	Ferric nitrate nonahydrate (FeN ₃ O ₉ ·9H ₂ O)	3.1368
Zn	Zinc nitrate hexahydrate (ZnN ₂ O ₆ ·6H ₂ O)	1.9867

- นำสารแขวนลอยที่ได้ไประเหยน้ำออกที่อุณหภูมิ 80°C เป็นเวลา 5 ชั่วโมง
- นำของแข็งที่ได้ไปอบในตู้อบที่อุณหภูมิ 110°C เป็นเวลา 24 ชั่วโมง
- นำของแข็งที่ผ่านการอบมา Calcine ด้วยอากาศ 100 ml/min ที่ 550°C เป็นเวลา 6 ชั่วโมง จะได้ตัวเร่งปฏิกิริยาที่มีโลหะฝังอยู่

3.2.3 วัดสมบัติของตัวเร่งปฏิกิริยาด้วยเทคนิคต่อไปนี้

3.2.3.1 การวัดพื้นที่ผิวสัมผัส

การวัดพื้นที่ผิวสัมผัสนั้นทำโดยใช้การดูดซับทางกายภาพของก๊าซไนโตรเจนด้วยเครื่อง Micromeritics ASAP 2000 ขั้นตอนการวัดแบ่งเป็น 2 ขั้นตอน ดังนี้

ขั้นตอนการไล่ก๊าซ

- นำตัวอย่างปริมาณ 0.3 กรัมใส่ในที่เก็บตัวอย่าง และนำที่เก็บตัวอย่างไปต่อกับแท่นไล่ก๊าซของเครื่องมือ
- ในช่วงทำสุญญากาศ ที่เก็บตัวอย่างถูกให้ความร้อนจนถึง 90°C ด้วยอัตราการเพิ่มอุณหภูมิ 2°C/min และคงไว้เป็นเวลานาน 1 ชั่วโมง ภายใต้การไหลของฮีเลียม
- ในช่วงให้ความร้อน ที่เก็บตัวอย่างถูกให้ความร้อนจนถึง 200°C ด้วยอัตราการเพิ่มอุณหภูมิ 2°C/min และคงไว้เป็นเวลานาน 1 ชั่วโมง ภายใต้การไหลของฮีเลียม

ขั้นตอนการวิเคราะห์

- ถอดที่เก็บตัวอย่างออกจากแท่นไล่ก๊าซที่เก็บตัวอย่างและนำไปต่อกับแท่นวิเคราะห์ของเครื่องมือ
- ทำการวิเคราะห์ด้วยการดูดซับไนโตรเจนที่อุณหภูมิของไนโตรเจนเหลว และบันทึกไอโซเทอร์มที่ได้

3.2.3.2 X-Ray Diffraction (XRD)

เฟสของสารตัวอย่างวิเคราะห์โดยใช้เครื่อง X-Ray Diffractometer ในที่นี้ใช้เครื่อง Siemens รุ่น D5000 X-Ray Diffractometer โดยใช้ การแผ่รังสีของ $\text{CuK}\alpha$ ร่วมกับ Ni ซึ่งทำหน้าที่ตัวกรอง ใช้มุม 2θ ในช่วง $20 - 80^\circ$ โดยมีความละเอียด 0.04°

3.2.3.3 วัดค่าความเป็นกรดของพื้นผิว

ศึกษาความเป็นกรดของสารตัวอย่างจากการดูดซับ Pyridine โดยใช้เครื่อง GC9A แบบ FID โดยตั้งเครื่อง GC9A แบบ FID ที่ภาวะดังต่อไปนี้

อัตราการไหลของไนโตรเจน	30 ml/min
อุณหภูมิคอลัมน์	150°C
อุณหภูมิ Detector	180°C
อุณหภูมิ Injector	180°C

แล้วทำการวัดตามขั้นตอนต่อไปนี้

1. บรรจุตัวอย่าง 0.02 g ลงในคอลัมน์
2. ฉีด Pyridine 0.1 ml และวัด peak area อย่างต่อเนื่องจนกระทั่งตัวอย่างดูดซับ Pyridine จนอิ่มตัว
3. คำนวณค่าความเป็นกรดของสารตัวอย่างจาก Total peak area ของการดูดซับ Pyridine

3.2.3.4 วัดค่าความเป็นเบส

ศึกษาความเป็นเบสของสารตัวอย่างจากการดูดซับ Maleic Anhydride โดยใช้เครื่อง GC9A แบบ FID โดยตั้งเครื่อง GC9A แบบ FID ที่ภาวะดังต่อไปนี้

อัตราการไหลของไนโตรเจน	30 ml/min
อุณหภูมิคอลัมน์	250°C
อุณหภูมิ Detector	300°C
อุณหภูมิ Injector	300°C

แล้วทำการวัดตามขั้นตอนต่อไปนี้

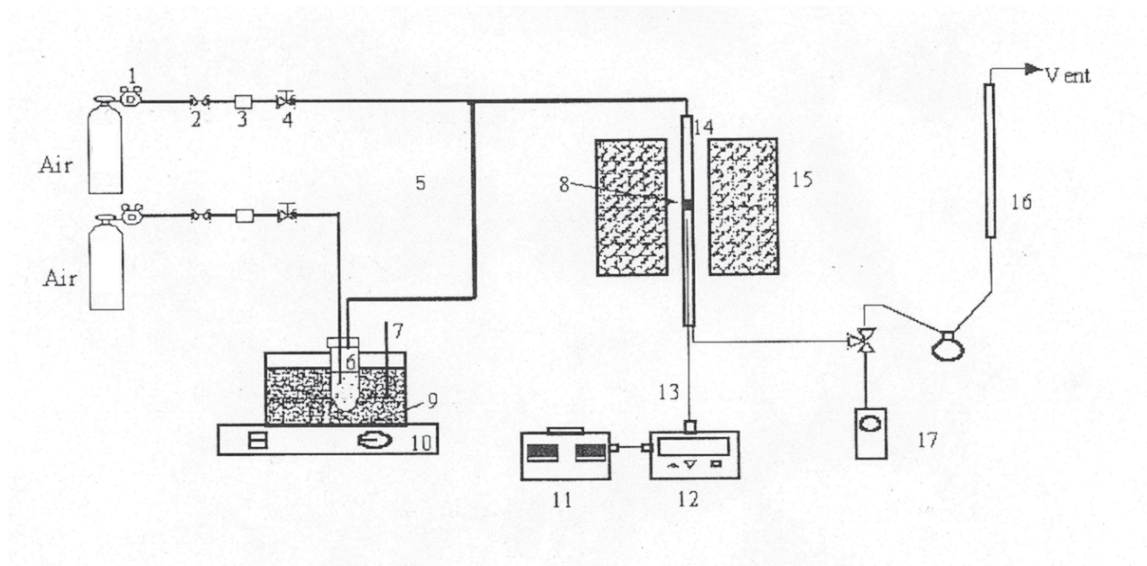
1. บรรจุสารตัวอย่าง 0.03 g ลงในคอลัมน์
2. ฉีด Maleic Anhydride เข้มข้น 0.104 g/ml ปริมาณ $0.3\text{ }\mu\text{l}$ และวัด peak area อย่างต่อเนื่องจนกระทั่งสารตัวอย่างดูดซับ Maleic Anhydride จนอิ่มตัว
3. คำนวณค่าความเป็นเบสของสารตัวอย่างจาก Total area peak ของการดูดซับ Maleic Anhydride

3.2.3.5 การหาค่าประกอบโลหะของตัวเร่งปฏิกิริยา

การหาค่าประกอบของโลหะต่างๆในตัวเร่งปฏิกิริยาทำโดยใช้เครื่อง Perkin-Elmer Optical Emission Optima 2100 DV ตัวอย่างจะถูกย่อยด้วยสารละลายกรดและฟั่นออกมาทางหัวฉีด จากนั้นทำการกระตุ้นอะตอมโลหะด้วยพลาสมา และบันทึก emission spectrum

3.2.4 การวัดความว่องไวในการทำปฏิกิริยาด้วยการทดลองในเครื่องปฏิกรณ์ชนิด fixed-bed

ทำการวัดความว่องไวของตัวเร่งปฏิกิริยาด้วยระบบที่แสดงในรูปข้างล่าง



- | | | |
|----------------------------|----------------------------------|--------------------|
| 1. Pressure Regulator | 2. On-Off valve | 3. Gas Filter |
| 4. Metering Valve | 5. Heating Line | 6. Saturator |
| 7. Thermometer | 8. Catalyst Bed | 9. Sand Bath |
| 10. Stirring Controller | 11. Variable Voltage Transformer | |
| 12. Temperature Controller | 13. Thermocouple | 14. Reactor |
| 15. Furnace | 16. Flow Meter | 17. Sampling Point |

รูปที่ 1 ระบบเครื่องปฏิกรณ์

เครื่องปฏิกรณ์นี้จัดทำมาจาก 3/8" stainless steel tube จุดที่เก็บสารตัวอย่างเพื่อนำมาทดสอบวิเคราะห์อยู่บริเวณด้านบนและด้านล่างเบดตัวเร่งปฏิกิริยา ซึ่งตัวเร่งปฏิกิริยานี้จะอยู่ระหว่างชั้นของ quartz wood อุณหภูมิของเครื่องปฏิกรณ์จะปรับได้ในช่วงระหว่าง 50-800°C การวิเคราะห์ Phthalic anhydride ในสารตั้งต้นและผลิตภัณฑ์ใช้ GC Shimadzu 9A

ติดตั้ง Detector แบบ FID และใช้ column Chromosorb W AW ใช้ N_2 (99.999%) เป็น carrier gas โดยตั้งค่าต่าง ๆ ดังนี้

อัตราการไหลของ N_2	30 ml/min
อุณหภูมิคอลัมน์	210°C
อุณหภูมิ Detector	250°C
อุณหภูมิ Injector	250°C

การวิเคราะห์ permanent gas ใช้เครื่อง GC Shimadzu 8A ติดตั้ง detector แบบ TCD โดยใช้คอลัมน์ molecular sieve 5A ในการแยก O_2 และ CO และ Porapak-Q ในการแยก CO_2

และนำ ใช้ He (99.999%) เป็น carrier gas โดยตั้งค่าต่าง ๆ ดังนี้

อัตราการไหลของ He	25 ml/min
อุณหภูมิคอลัมน์	100°C
อุณหภูมิ Detector	130°C
อุณหภูมิ Injector	130°C

3.3 ตัวเร่งปฏิกิริยาสำหรับปฏิกิริยาเลือกเติมไฮโดรเจน

3.3.1 การเตรียมตัวเร่งปฏิกิริยาแพลเลเดียม-ซิลเวอร์บนตัวรองรับอะลูมินา

3.3.1.1 เตรียมตัวรองรับอะลูมินา

1. บดอะลูมินา (CS-303) แล้วร่อนผ่านตะแกรง 40/60 เมช
2. ล้างอะลูมินาที่บดได้ด้วยน้ำกลั่นหลายๆ ครั้ง เพื่อกำจัดฝุ่น และสารปนเปื้อน
3. อบแห้งเพื่อไล่ความชื้นที่อุณหภูมิ 110°C เป็นเวลา 12 ชั่วโมง
4. เผาเหลืออยู่ในอากาศนิ่ง ที่ 300°C เป็นเวลา 2 ชั่วโมง
5. ร่อนผ่านตะแกรง 40/60 เมช อีกครั้ง แล้วเก็บใส่ขวดปิดผนึก

3.3.1.2 เตรียมสารละลายสต็อกของแพลเลเดียม และซิลเวอร์

ละลาย $Pd(NO_3)_2$ 0.1 g ในน้ำ 25 ml และละลาย $AgNO_3$ 0.5 g ในน้ำ 25 ml แล้วเก็บใส่ขวดปิดผนึก

3.3.1.3 เตรียมตัวเร่งปฏิกิริยาแพลเลเดียม-ซิลเวอร์บนตัวรองรับอะลูมินา

1. ชั่งอะลูมินา 2 g ใส่ในขวดรูปชมพู่ขนาด 100 ml
2. เตรียมสารละลายแพลเลเดียมจากสารละลายสต็อก โดยคำนวณปริมาณแพลเลเดียมที่ใช้ให้ได้เปอร์เซ็นต์ตามต้องการ เพื่อใช้กับอะลูมินา 2 g แล้วเติมน้ำให้สารละลายแพลเลเดียมมีปริมาตรรวมเท่ากับ 1 ml

3. หยดสารละลายแพลเลเดียมที่ได้จากข้อ 2 ลงบนอะลูมินาเป็นหย่อมๆ ให้ทั่วถึง แล้วเผาเพื่อให้เกิดการกระจายตัวที่ดีของแพลเลเดียมบนอะลูมินา ทำซ้ำจนกว่าสารละลายแพลเลเดียมจะหมด
4. ปลอ่ยให้ของผสมที่ได้จากข้อ 3 เกิดการกระจายตัว โดยทิ้งไว้ในภาชนะที่อุณหภูมิห้อง เป็นเวลา 6 ชั่วโมง
5. อบแห้ง ที่ 110°C เป็นเวลา 12 ชั่วโมง
6. เผาเหลือเ้าในอากาศไหล ที่ 500°C เป็นเวลา 2 ชั่วโมง ที่อัตราการไหล 100 ml/min และอัตราการเพิ่มอุณหภูมิ $10^{\circ}\text{C}/\text{min}$
7. นำของผสมที่ได้จากข้อ 6 มาทำซ้ำในข้อ 2 ถึง 5 แต่เปลี่ยนจากการใช้สารละลายแพลเลเดียม เป็นสารละลายซิลเวอร์
8. เผาเหลือเ้าในอากาศไหล ที่ 370°C เป็นเวลา 1 ชั่วโมง ที่อัตราการไหล 100 ml/min และอัตราการให้ความร้อน $10^{\circ}\text{C}/\text{min}$
9. แล้วเก็บใส่ขวดปิดผนึก เพื่อนำไปใช้ต่อไป

3.3.2 ทดสอบความว่องไวของตัวเร่งปฏิกิริยา

1. บรรจุตัวเร่งปฏิกิริยาลงในเครื่องปฏิกรณ์โดยใช้ตัวเร่งปฏิกิริยา 0.5 g
2. ไล่อากาศที่เหลืออยู่ในเครื่องปฏิกรณ์ด้วยแก๊ส Ar เป็นเวลา 10 นาที
3. ริคิวซ์ด้วย H_2 100 ml/min ที่อุณหภูมิ 150°C เป็นเวลา 2 ชั่วโมง และอัตราการเพิ่มอุณหภูมิ $10^{\circ}\text{C}/\text{min}$
4. ไล่ H_2 ที่เหลืออยู่ในเครื่องปฏิกรณ์ด้วยแก๊ส Ar เป็นเวลา 10 นาที
5. ลดอุณหภูมิไปที่อุณหภูมิในการปรับสภาพ ซึ่งอยู่ในช่วง $40\text{-}90^{\circ}\text{C}$ โดยใช้แก๊สปรับสภาพเช่น CO CO_2 O_2 NO และ N_2O เป็นต้น ถัดเข้าไปในทางเข้าของเครื่องปฏิกรณ์ แล้วคงอุณหภูมิไว้เป็นเวลา 10 นาที จากนั้นลดอุณหภูมิลงไปที่อุณหภูมิห้อง
6. ปรับอัตราการไหลเชิงปริมาตรของแก๊สดังตั้งผสม ซึ่งมีส่วนประกอบของ C_2H_2 0.716 vol% H_2 0.823 vol% C_2H_6 33.707 vol% และ C_2H_4 ให้มีอัตราการไหลรวม 15 ml/min เพื่อทำการทดสอบความสามารถในการเกิดปฏิกิริยา
7. ทำการทดสอบก๊าซสารตั้งต้นที่อุณหภูมิ $40\text{-}90^{\circ}\text{C}$ โดยแต่ละอุณหภูมิจะทำการศึกษาเมื่อระบบเข้าสู่ภาวะคงตัวแล้ว นั่นคือเมื่อเวลาผ่านไปแล้วประมาณ 20 นาที

8. ทำการวิเคราะห์ก๊าซที่ไหลออกมาโดยใช้ GC Shimadzu-9A ในการวิเคราะห์แก๊ส CH_4 C_2H_2 C_2H_4 และ C_2H_6 โดยใช้คอลัมน์ carbosieve S-II และใช้ GC Shimadzu-8A ในการวิเคราะห์ก๊าซ H_2 โดยใช้คอลัมน์ molecular sieve 5A

3.3.3 การวิเคราะห์สมบัติของตัวเร่งปฏิกิริยา

ทำการวัดสมบัติด้วยเครื่องมือต่าง ๆ ดังต่อไปนี้

3.3.3.1 การดูดซับก๊าซคาร์บอนมอนอกไซด์ (CO adsorption)

1. บรรจุตัวเร่งปฏิกิริยาในเครื่องปฏิกรณ์ขนาดเล็กจำนวน 0.3-0.5 g
2. ปรับก๊าซ He โดยให้ He ไหลผ่านเครื่องปฏิกรณ์ที่อัตราการไหล 30 ml/min เพื่อเข้าไปในเครื่อง GC แบบ TCD โดยทำการวัดอัตราการไหลของก๊าซ He ทั้ง reference line และ line ที่ต้องการทดสอบ
3. ปรับก๊าซ H_2 ให้มีอัตราการไหล 100 ml/min
4. เปิดก๊าซ He ให้ไหลผ่านเครื่องปฏิกรณ์เพื่อไล่อากาศที่หลงเหลืออยู่ เป็นเวลา 10 นาที
5. เปลี่ยนจากก๊าซ He เป็นก๊าซ H_2 เพื่อทำการรีดิวส์ โดยเพิ่มความร้อนที่อัตราการเพิ่มอุณหภูมิ $10^\circ\text{C}/\text{min}$ จนอุณหภูมิถึง 150°C คงอุณหภูมิ 150°C เป็นเวลา 2 ชั่วโมง ทำการลดอุณหภูมิลงมาที่อุณหภูมิห้อง โดยใช้ก๊าซ He ไหลผ่านตลอดการลดอุณหภูมิ
6. ฉีดก๊าซ CO ที่ละ 50 μl พร้อมทั้งสังเกตสัญญาณจาก TCD
7. ฉีดซ้ำจนตัวเร่งปฏิกิริยาดูดซับปริมาณก๊าซ CO จนกระทั่งอิ่มตัว นำผลที่ได้มาคำนวณหาปริมาณก๊าซ CO ทั้งหมดที่ถูกดูดซับ

3.3.3.2 XPS (X-ray photoelectron spectroscopy)

1. นำตัวเร่งปฏิกิริยาที่ได้หลังจากการทำการทดสอบไปเตรียม grid โดยการบดตัวเร่งปฏิกิริยาในบรรยากาศ N_2 เพื่อให้มีการกระจายตัวของผงตัวเร่งปฏิกิริยาอย่างสม่ำเสมอ โดยใช้ double-side adhesive tape ติดทั้งสองข้าง
2. นำตัวอย่างที่เตรียมไปวางใน Kratos XSAM, XPS Spectrometer
3. สารตัวอย่างจะถูกส่งยังช่องที่ใช้ในการเตรียม ซึ่งเป็นระบบที่มีความดันต่ำกว่า 10^{-7} Torr เป็นระบบสุญญากาศ
4. ในการวิเคราะห์ธาตุต่างๆที่อยู่ในสารตั้งต้น จะใช้ช่วงในการ scan ที่กว้าง โดยใส่พลังงานมีค่าประมาณ 160 eV และใช้เวลาในการเก็บอิเล็กตรอนที่เคลื่อนออกจากผิว 300 วินาทีต่อ 1 eV

3.3.3.3 TPR (Temperature-programmed reduction)

1. บรรจุตัวเร่งปฏิกิริยา 1 กรัม ใน TPR pyrex cell
2. ปรับก๊าซ Ar ให้มีอัตราไหล 20 ml/min โดยให้ไหลอยู่ในระบบ
3. ให้ความร้อนสารตัวอย่างโดยให้ก๊าซ Ar ไหลตลอดเวลา โดยให้ความร้อนจนมีอุณหภูมิ 200°C และไว้เป็นเวลา 1 ชั่วโมงเพื่อไล่ก๊าซที่สารตัวอย่างดูดซับไว้
4. การทำ TPR ของ oxidized sample จะใช้ $10\%\text{H}_2/\text{Ar}$ เป็น reducing agent โดยมีอัตราการให้ความร้อน $20^{\circ}\text{C}/\text{min}$ โดยจะให้ความร้อนไปจนถึงอุณหภูมิ 500°C และทำการคงอุณหภูมิไว้เป็นเวลา 10 นาที

3.3.3.4 TPD (Temperature-programmed desorption)

1. ทำการรีดิวซ์สารตัวอย่างที่อุณหภูมิ 150°C เป็นเวลา 2 ชั่วโมง
2. เปลี่ยนเป็นก๊าซ Ar เพื่อใช้ในการลดอุณหภูมิไปที่อุณหภูมิห้อง
3. ก๊าซ H_2 จะดูดซับบนสารตัวอย่างก่อนที่จะมีก๊าซ Ar ไหลผ่าน
4. จะเกิด desorption spectra ระหว่างการเพิ่มอุณหภูมิที่อัตราการเพิ่ม $20^{\circ}\text{C}/\text{min}$

3.3.3.5 Fourier transform infrared spectroscopy

1. อัดตัวเร่งปฏิกิริยาให้มีเส้นผ่านศูนย์กลาง 20 mm จากนั้นใส่เข้าไปในเซลล์สำหรับใส่สารตัวอย่าง โดยจะมีใช้การดูดซับรังสีอินฟราเรดในการวิเคราะห์ ที่ค่าความละเอียดเท่ากับ 4 cm^{-1}
2. ตัวเร่งปฏิกิริยาจะถูกรีดิวซ์ในบรรยากาศ H_2 ณ อุณหภูมิ 150°C เป็นเวลา 2 ชั่วโมง หลังจากนั้นจะทำการลดอุณหภูมิไปที่อุณหภูมิห้อง โดยจะทำการเปลี่ยนก๊าซจากก๊าซ H_2 เป็น Ar ในการลดอุณหภูมิ
3. สำหรับตัวเร่งปฏิกิริยาที่มีการเตรียมพื้นที่ผิวของตัวเร่งปฏิกิริยาก่อนใช้ในปฏิกิริยา ในการลดอุณหภูมิหลังการรีดิวซ์ จะทำการเปลี่ยนก๊าซจากก๊าซ H_2 เป็น Ar ในขณะที่ลดอุณหภูมิ จนกระทั่งมีอุณหภูมิถึงอุณหภูมิที่ต้องการใช้ในการเตรียมพื้นที่ผิว
4. ก๊าซที่ใช้ในการเตรียมพื้นที่ผิว ได้แก่ CO , CO_2 , NO , และ N_2O จะถูกฉีดเข้าไปในระบบที่อุณหภูมิตั้งแต่เป็นเวลา 10 นาที ก่อนทำการลดอุณหภูมิจนไปถึงอุณหภูมิห้อง
5. จากนั้นจึงทำการวัดค่าการดูดซับรังสีอินฟราเรด โมเลกุลของก๊าซต่างชนิดกันจะให้ตำแหน่งในการดูดซับรังสีอินฟราเรด ณ ตำแหน่งที่แตกต่างกัน

3.3.3.6 การวัดพื้นที่ผิวสัมผัส

การวัดพื้นที่ผิวสัมผัสนั้นทำโดยใช้การดูดซับทางกายภาพของก๊าซในโตรเจนด้วยเครื่อง Micromeritics ASAP 2000 ขั้นตอนการวัดแบ่งเป็น 2 ขั้นตอน ดังนี้

ขั้นตอนการไล้ก๊าซ

1. นำตัวอย่างปริมาณ 0.3 กรัมใส่ในที่เก็บตัวอย่าง และนำที่เก็บตัวอย่างไปต่อกับแท่นไล้ก๊าซของเครื่องมือ
2. ในช่วงทำสุญญากาศ ที่เก็บตัวอย่างถูกให้ความร้อนจนถึง 90°C ด้วยอัตราการเพิ่มอุณหภูมิ $2^{\circ}\text{C}/\text{min}$ และคงไว้เป็นเวลานาน 1 ชั่วโมง ภายใต้การไหลของฮีเลียม
3. ในช่วงให้ความร้อน ที่เก็บตัวอย่างถูกให้ความร้อนจนถึง 200°C ด้วยอัตราการเพิ่มอุณหภูมิ $2^{\circ}\text{C}/\text{min}$ และคงไว้เป็นเวลานาน 1 ชั่วโมง ภายใต้การไหลของฮีเลียม

ขั้นตอนการวิเคราะห์

1. ถอดที่เก็บตัวอย่างออกจากแท่นไล้ก๊าซที่เก็บตัวอย่างและนำไปต่อกับแท่นวิเคราะห์ของเครื่องมือ
2. ทำการวิเคราะห์ด้วยการดูดซับไนโตรเจนที่อุณหภูมิของไนโตรเจนเหลว และบันทึกไอโซเทอร์มที่ได้

3.4 ตัวเร่งปฏิกิริยาเพื่อกำจัดมลพิษในอากาศ

3.4.1 การเตรียมตัวเร่งปฏิกิริยาโลหะ

8.4.1.1 ตัวอย่างการเตรียมตัวเร่งปฏิกิริยาแพลทินัมบนตัวรองรับอะลูมินา

ก. เตรียมตัวรองรับอะลูมินา

1. บดอะลูมินา (NKH-3) แล้วร่อนผ่านตะแกรง 40/60 เมช
2. ล้างอะลูมินาที่บดได้ด้วยน้ำกลั่นหลายๆ ครั้ง เพื่อกำจัดฝุ่น และสารปนเปื้อน
3. อบแห้งเพื่อไล่น้ำ ที่อุณหภูมิ 110°C เป็นเวลา 12 ชั่วโมง
4. เผาเหลือเถ้าในอากาศนิ่ง ที่อุณหภูมิ 300°C เป็นเวลา 2 ชั่วโมง
5. ร่อนผ่านตะแกรง 40/60 เมช อีกครั้ง แล้วเก็บใส่ขวดปิดผนึก

ข. เตรียมสารละลายสต็อก (Stock solution)

ละลาย $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$ 1 กรัมในน้ำกลั่น 25 ml แล้วเก็บใส่ขวดปิดผนึก

ค. เตรียมตัวเร่งปฏิกิริยาแพลทินัมบนตัวรองรับอะลูมินา

1. เตรียมสารละลายแพลทินัมจากสารละลายสต็อก โดยคำนวณปริมาณแพลทินัมที่ใช้ให้ได้เปอร์เซ็นต์ตามต้องการ เพื่อใช้กับอะลูมินา 2 g แล้วเติมน้ำกลั่นให้

สารละลาย

แพลทินัมมีปริมาตรรวมเท่ากับ 2 ml

2. ชั่งอะลูมินา 2 g ใส่ในขวดรูปชมพู่ขนาด 100 ml

3. หยดสารละลายแพลทินัมที่ได้จากข้อ 1 ลงบนอะลูมินาเป็นหย่อมๆ ให้ทั่วถึง แล้วเขย่า เพื่อให้เกิดการกระจายตัวที่ดีของแพลทินัมบนอะลูมินา ทำซ้ำจนกว่าสารละลาย

แพลทินัมจะหมด

4. ปลอ่ยให้ของผสมที่ได้จากข้อ 3 เกิดการกระจายตัว โดยทิ้งไว้ในภาชนะที่อุณหภูมิห้อง เป็นเวลา 6 ชั่วโมง

5. อบแห้ง ที่อุณหภูมิ 110°C เป็นเวลา 12 ชั่วโมง

6. เผาเหลือเ้าในอากาศไหล ที่อุณหภูมิ 500°C เป็นเวลา 3 ชั่วโมง ด้วยอัตราการไหล 100 ml/min และอัตราการให้ความร้อน 10°C/min

7. เก็บใส่ขวดปิดผนึก เพื่อนำไปใช้ต่อไป

3.4.1.2 ตัวอย่างการเตรียมตัวเร่งปฏิกิริยาแวนเดียมบนตัวรองรับไทเทเนียมออกไซด์

1. เตรียมตัวรองรับ TiO_2 โดยการเผาเหลือเ้าในอากาศที่ 300°C นาน 3 ชั่วโมง

2. เตรียมของผสมของตัวรองรับ TiO_2 และสารละลาย NH_4VO_3 ใส่ในขวดรูปชมพู่ขนาด 250 ml โดยคำนวณปริมาณแวนเดียมที่ใช้ให้ได้เปอร์เซ็นต์ตามต้องการ แล้วเติมน้ำกลั่นลงไปให้มีปริมาตรรวมเท่ากับ 50 ml

3. กวนของผสมอย่างต่อเนื่อง ที่อุณหภูมิ 70°C จนกระทั่งน้ำระเหยหมด

4. อบแห้ง ที่อุณหภูมิ 110°C เป็นเวลา 12 ชั่วโมง

5. เผาเหลือเ้าในอากาศไหล ที่อุณหภูมิ 380°C เป็นเวลา 3 ชั่วโมง ด้วยอัตราการไหล 100 ml/min และอัตราการให้ความร้อน 10°C/min

6. เก็บใส่ขวดปิดผนึก เพื่อนำไปใช้ต่อไป

3.4.2 ทดสอบประสิทธิภาพของตัวเร่งปฏิกิริยา

3.4.2.1 การทดสอบความว่องไวของตัวเร่งปฏิกิริยา

1. บรรจุตัวเร่งปฏิกิริยาลงในเครื่องปฏิกรณ์ขนาดเล็ก 0.1 ถึง 0.5 g

2. ปรับสภาพของตัวเร่งปฏิกิริยาให้พร้อมใช้งาน โดยขึ้นอยู่กัขนิดของตัวเร่งปฏิกิริยา

และวัตถุประสงค์ของการทดสอบ ตัวอย่างเช่น

- ตัวเร่งปฏิกิริยาแพลทินัมบนตัวรองรับอะลูมินา จะต้องปรับสภาพด้วยการรีดิวซ์ในไฮโดรเจน ที่ 500°C เป็นเวลา 1 ชั่วโมง ด้วยอัตราการไหลเชิงปริมาตร 100 ml/min และอัตราการให้ความร้อน $10^{\circ}\text{C}/\text{min}$ เพื่อเปิดไซส์ที่ว่องไวของตัวเร่งปฏิกิริยา แล้วตามด้วยการออกซิไดซ์ใน 10 เปอร์เซ็นต์ของออกซิเจนในฮีเลียม ที่อุณหภูมิ 500°C เป็นเวลา 1 ชั่วโมง ด้วยอัตราการไหลเชิงปริมาตร 100 ml/min และอัตราการให้ความร้อน $10^{\circ}\text{C}/\text{min}$

3. ปรับอัตราการไหลเชิงปริมาตรของแก๊สตั้งต้นผสม ให้ได้ตามต้องการ ตัวอย่างเช่น

- การทดสอบตัวเร่งปฏิกิริยาแพลทินัมบนตัวรองรับอะลูมินา สำหรับปฏิกิริยารีดักชันแบบเลือกเกิดของ NO ด้วย C_3H_6 ในภาวะที่มีออกซิเจนมากเกินไป จะใช้แก๊สผสมของ NO 1000 ppm C_3H_6 1000 ppm O_2 5 mol% และส่วนที่เหลือเป็น He โดยมีอัตราการไหลรวมเป็น 200 ml/min

- การทดสอบตัวเร่งปฏิกิริยาแพลทินัมบนตัวรองรับอะลูมินา สำหรับปฏิกิริยาการกำจัดแก๊สเสียที่ปล่อยออกมาจากเครื่องยนต์แก๊สโซลีน จะใช้แก๊สผสมของ NO 500 ppm CO 3000 ppm C_3H_8 2150 ppm O_2 1.2 mol% และส่วนที่เหลือ He โดยมีอัตราการไหลเชิงปริมาตรรวมเป็น 141 ml/min

4. ทดสอบความว่องไวของตัวเร่งปฏิกิริยา ด้วยวิธีการทำปฏิกิริยาแบบโปรแกรมอุณหภูมิ กำหนดช่วงอุณหภูมิในการศึกษาอยู่ระหว่าง 50 ถึง 800°C โดยทำการให้ความร้อน แบบขั้นบันได แต่ละอุณหภูมิ จะทำการเก็บแก๊สตัวอย่างเมื่อระบบเข้าสู่สภาวะคงตัว

5. ทำการเก็บและวิเคราะห์แก๊สที่ปล่อยออกมาจากเครื่องปฏิกรณ์ โดยใช้เครื่อง GC แบบ TCD ร่วมกับคอลัมน์ชนิด MS-5A และ Porapak QS

3.4.2.2 การทดสอบความทนทานของตัวเร่งปฏิกิริยาต่อน้ำหรือ SO_2

- การทดสอบแบบ Ex-situ

1. ทำการปรับสภาพตัวเร่งปฏิกิริยาก่อนการทดสอบความว่องไว ดังนี้

ต้องการทดสอบความทนทานของตัวเร่งปฏิกิริยาซีโอไลต์ต่อน้ำ จะต้องปรับสภาพด้วย 10% ของไอน้ำในฮีเลียม ที่อุณหภูมิ 600°C เป็นเวลา 24 ชั่วโมง ด้วยอัตราการไหล 170 ml/min และอัตราการให้ความร้อน $10^{\circ}\text{C}/\text{min}$ (ช่วงการให้ความร้อนทำในฮีเลียม)

ต้องการทดสอบความทนทานของตัวเร่งปฏิกิริยาแพลทินัมบนตัวรองรับอะลูมินาต่อ SO_2 จะต้องปรับสภาพด้วยแก๊สผสมของ SO_2 500 ppm O_2 5%

และส่วนที่เหลือเป็นฮีเลียม ที่ 480°C เป็นเวลา 10 ชั่วโมง ด้วยอัตราการไหล 100 ml/min และอัตราการให้ความร้อน $10^{\circ}\text{C}/\text{min}$ (ช่วงการให้ความร้อนทำใน O_2 10% ในฮีเลียม)

2. หลังจากการปรับสภาพแล้ว ทำการทดสอบความว่องไวของตัวเร่งปฏิกิริยาตามขั้นตอนในข้อ 8.4.2.1 ต่อไป

- การทดสอบแบบ In-situ

ทำการทดลองเหมือนกับ การทดสอบความว่องไวของตัวเร่งปฏิกิริยาในข้อ 8.4.2.1 แต่เปลี่ยนแปลงในขั้นตอนที่ 4 และ 5 โดยทดสอบความว่องไวของตัวเร่งปฏิกิริยา ด้วยวิธีการทำปฏิกิริยาแบบสลับเปลี่ยนวงจรดังนี้

1. เพิ่มอุณหภูมิด้วยฮีเลียมไปที่อุณหภูมิในการทดสอบ (ขึ้นอยู่กับชนิดของตัวเร่งปฏิกิริยา และสถานะในการเกิดปฏิกิริยา)
2. เปลี่ยนแก๊สจาก He เป็นแก๊สดังต้นผสมที่ไม่มีน้ำหรือ SO_2 อยู่ แล้วคงอุณหภูมิไว้จนระบบเข้าสู่สภาวะคงตัว ทำการเก็บและวิเคราะห์แก๊สที่ปล่อยออกมาจากเครื่องปฏิกรณ์โดยใช้เครื่อง GC แบบ TCD ร่วมกับคอลัมน์ชนิด MS-5A และ Porapak QS
3. ปล่อยน้ำและ/หรือ SO_2 ผสมกับแก๊สดังต้น คงอุณหภูมิไว้จนระบบเข้าสู่สภาวะคงตัว ทำการเก็บ และวิเคราะห์แก๊สที่ปล่อยออกมาจากเครื่องปฏิกรณ์ โดยวิธีเดียวกับข้อ 2
4. ปิดน้ำและ/หรือ SO_2 ผสมกับแก๊สดังต้น คงอุณหภูมิไว้จนระบบเข้าสู่สภาวะคงตัว ทำการเก็บ และวิเคราะห์แก๊สที่ปล่อยออกมาจากเครื่องปฏิกรณ์ โดยวิธีเดียวกับข้อ 2
5. ทำซ้ำในข้อ 3 และ 4 หลายๆ ครั้งตามต้องการ

3.4.2.3 การทดสอบความสามารถในการฟื้นฟูสภาพของตัวเร่งปฏิกิริยา

1. ทำการปรับสภาพตัวเร่งปฏิกิริยาด้วย 5% NH_3 ใน N_2 ที่อุณหภูมิห้อง เป็นเวลา 0.5 ถึง 2 ชั่วโมง ด้วยอัตราการไหลเชิงปริมาตร 4 ml/min
2. นำตัวเร่งปฏิกิริยาที่ได้จากข้อ 1. มาทำคลอรีนชันแบบเปียก โดยผ่านอากาศขึ้นไบนตัวเร่งปฏิกิริยา ในช่วงอุณหภูมิ 450 ถึง 550°C พร้อมด้วยการฉีดกรดอินทรีย์ของคลอรีน ปริมาณ 15 ถึง 50 μl แล้วทำการลดอุณหภูมิจนถึงอุณหภูมิห้อง
3. นำตัวเร่งปฏิกิริยาที่ได้จากข้อ 2. มาทำการรีดิวซ์ด้วย H_2 ที่ 500°C เป็นเวลา 1 ชั่วโมงด้วยอัตราการไหลเชิงปริมาตร 30 ml/min และอัตราการให้ความร้อน $10^{\circ}\text{C}/\text{min}$ แล้วทำการลดอุณหภูมิจนถึงอุณหภูมิห้อง

4. หลังจากการปรับฟื้นฟูสภาพของตัวเร่งปฏิกิริยาแล้ว ทำการทดสอบความว่องไวของตัวเร่งปฏิกิริยาตามขั้นตอนในข้อ 8.4.2.1 ต่อไป

3.4.2.4 การทดสอบเพื่อศึกษากลไกการเกิดปฏิกิริยา

1. การใช้เทคนิคทรานเซียนส์

สามารถแบ่งการทดลองออกได้เป็น 2 ขั้นตอน ได้แก่ ขั้นตอนที่ทดสอบโดยไม่มีตัวเร่งปฏิกิริยา และขั้นตอนการทดสอบปฏิกิริยา

ขั้นตอนที่ 1: การทดลองแบบไม่มีตัวเร่งปฏิกิริยา

ทดสอบการตอบสนองทางพลศาสตร์ของเครื่องปฏิกรณ์ขนาดเล็ก โดยไม่ใส่ตัวเร่งปฏิกิริยา ด้วยการเปลี่ยนแก๊สเข้าจาก N_2 เป็น NO 1.2 mol% ผ่านเครื่องปฏิกรณ์ โดยใช้อัตราการไหลรวม 50 ml/min ทำให้แก๊สมีเวลาในการไหลจากวาล์วเข้าสู่เครื่องวิเคราะห์อินฟราเรด เป็นเวลาประมาณ 12 วินาที ที่อุณหภูมิห้อง หมายเหตุ : เครื่องสามารถวัดสัญญาณการดูดกลืนลำแสงอินฟราเรด ของ NO NO_2 และ N_2O CO_2 และ C_3H_8 ในเวลาเดียวกัน แต่ไม่สามารถวัด N_2 และ O_2 ได้

ขั้นตอนที่ 2: การทดสอบปฏิกิริยา

1. บรรจุตัวเร่งปฏิกิริยาขนาด 10/20 เมช ประมาณ 1.2 g ลงไปในเครื่องปฏิกรณ์ สารตั้งต้นถูกปรับความเข้มข้นด้วยไนโตรเจน เพื่อใช้เป็นสารป้อนเข้าเครื่องปฏิกรณ์ อัตราการไหลรวมเท่ากับ 50 ml/min ซึ่งมีค่าองค์ประกอบของแก๊สในการทดลอง คือ

NO 1.2% ใน N_2

NO 0.5% O_2 12% ใน N_2

NO 0.5% C_3H_8 0.4% ใน N_2

NO 0.5% C_3H_8 0.4% O_2 12% ใน N_2

2. ทดสอบปฏิกิริยา ในช่วงอุณหภูมิ 300 ถึง 400°C โดยก่อนจะทำการทดลองทุกครั้งจะปล่อย N_2 ที่อัตราการไหล 50 ml/min ที่อุณหภูมิ 450°C เป็นเวลา 1 ชั่วโมง เพื่อจะกำจัดน้ำและองค์ประกอบที่เหลืออยู่บนพื้นผิวของตัวเร่งปฏิกิริยา

3. ลดอุณหภูมิลงไปที่อุณหภูมิของปฏิกิริยา แก๊สตั้งต้นผสมจะป้อนเข้ามาแทน N_2 หลังจากที่มีการดูดซับของแก๊สเริ่มคงที่ สารป้อนที่เข้าสู่เครื่องปฏิกรณ์จะเปลี่ยนไปเป็น N_2 อีกครั้งอย่างทันทีทันใด เพื่อที่จะทำการศึกษาลักษณะพลศาสตร์ในส่วนในช่วงของการป้อนสารตั้งต้นเข้า และลดการป้อนสารตั้งต้นเข้าเครื่องปฏิกรณ์

2. การใช้เทคนิคแบบโปรแกรมอุณหภูมิ

สามารถแบ่งการทดลองแบบพื้นฐานออกได้เป็น 3 ขั้นตอน ได้แก่
ขั้นตอนการสร้างสปีชีส์บนพื้นผิวของตัวเร่งปฏิกิริยา ขั้นตอนการสลายตัว/หลุด
ออกแบบโปรแกรมอุณหภูมิ และ ขั้นตอนการออกซิเดชันแบบโปรแกรมอุณหภูมิ
ขั้นตอนที่ 1: การสร้างสปีชีส์บนพื้นผิวของตัวเร่งปฏิกิริยา

1. บรรจุตัวเร่งปฏิกิริยา ลงในเครื่องปฏิกรณ์ขนาดเล็ก โดยใช้ตัวเร่งปฏิกิริยา 0.1 ถึง 0.5 g ขึ้นอยู่กับการกำหนดภาวะของปฏิกิริยา
2. ปรับสภาพของตัวเร่งปฏิกิริยาให้พร้อมใช้งาน โดยขึ้นอยู่กับชนิดของตัวเร่งปฏิกิริยา และวัตถุประสงค์ของการทดสอบ
3. ปรับอัตราการไหลเชิงปริมาตรของแก๊สดังต้นผสม ให้ได้ตามต้องการ
4. สร้างสปีชีส์บนพื้นผิวของตัวเร่งปฏิกิริยา โดยปล่อยให้เกิดปฏิกิริยาที่อุณหภูมิคงที่ตามต้องการ แต่กำหนดระยะเวลาของการเกิดปฏิกิริยาให้แน่นอน โดยทั่วไปจะหยุดการสร้างสปีชีส์ หลังจากระบบเข้าสู่สภาวะคงตัวแล้ว

ขั้นตอนที่ 2: การสลายตัว/หลุดออกแบบโปรแกรมอุณหภูมิ

เพิ่มอุณหภูมิจากอุณหภูมิห้อง ถึง 800°C ด้วย He โดยใช้อัตราการไหลเชิงปริมาตร 50 ml/min และอัตราการให้ความร้อน $5^{\circ}\text{C}/\text{min}$ ทำการเก็บและวิเคราะห์แก๊สที่ปล่อยออกมาจากเครื่องปฏิกรณ์ ทุกๆ 5 หรือ 10 นาที

ขั้นตอนที่ 3: การออกซิเดชันแบบโปรแกรมอุณหภูมิ

เพิ่มอุณหภูมิจากอุณหภูมิห้อง ถึง 800°C ด้วย 1% O_2 ใน He โดยใช้อัตราการไหลเชิงปริมาตร 50 ml/min และอัตราการให้ความร้อน $5^{\circ}\text{C}/\text{min}$ ทำการเก็บและวิเคราะห์แก๊สที่ปล่อยออกมาจากเครื่องปฏิกรณ์ ทุกๆ 5 นาที

3.4.3 ทำการวิเคราะห์สมบัติของตัวเร่งปฏิกิริยา

3.4.3.1 การวัดพื้นที่ผิวสัมผัส

การวัดพื้นที่ผิวสัมผัสนั้นทำโดยใช้การดูดซับทางกายภาพของก๊าซไนโตรเจนด้วยเครื่อง Micromeritics ASAP 2000 ขั้นตอนการวัดแบ่งเป็น 2 ขั้นตอน ดังนี้

ขั้นตอนการไล่ก๊าซ

1. นำตัวอย่างปริมาณ 0.3 กรัมใส่ในที่เก็บตัวอย่าง และนำที่เก็บตัวอย่างไปต่อกับแท่นไล่ก๊าซของเครื่องมือ
2. ในช่วงทำสุญญากาศ ที่เก็บตัวอย่างถูกให้ความร้อนจนถึง 90°C ด้วยอัตราการเพิ่มอุณหภูมิ $2^{\circ}\text{C}/\text{min}$ และคงไว้เป็นเวลานาน 1 ชั่วโมง ภายใต้การไหลของฮีเลียม

3. ในช่วงให้ความร้อน ที่เก็บตัวอย่างถูกให้ความร้อนจนถึง 200°C ด้วยอัตราการเพิ่มอุณหภูมิ $2^{\circ}\text{C}/\text{min}$ และคงไว้เป็นเวลานาน 1 ชั่วโมง ภายใต้การไหลของฮีเลียม

ขั้นตอนการวิเคราะห์

1. ถอดที่เก็บตัวอย่างออกจากแท่นไล่ก๊าซที่เก็บตัวอย่างและนำไปต่อกับแท่นวิเคราะห์ของเครื่องมือ
2. ทำการวิเคราะห์ด้วยการดูดซับไนโตรเจนที่อุณหภูมิของไนโตรเจนเหลว และบันทึกไอโซเทอร์มที่ได้

3.4.3.2 การวิเคราะห์ตำแหน่งวงไวและการกระจายตัวของโลหะบนตัวเร่งปฏิกิริยา

จำนวนตำแหน่งวงไวและการกระจายตัวของโลหะบนตัวเร่งปฏิกิริยานั้นวัดด้วยเทคนิคการดูดซับทางเคมีแบบเป็นจังหวะของคาร์บอนมอนอกไซด์โดยใช้เครื่อง Micromeritics Chemisorb 2750 (pulse chemisorptions system) ปริมาณของคาร์บอนมอนอกไซด์ที่ทราบถูกฉีดเข้าสู่ระบบที่อุณหภูมิห้อง ปริมาณคาร์บอนมอนอกไซด์ที่ไม่โดนดูดซับจะถูกวัดด้วย TCD การฉีดคาร์บอนมอนอกไซด์เป็นจังหวะจะทำให้ไปเรื่อยๆจนกระทั่งพื้นผิวของตัวเร่งปฏิกิริยาเกิดการอิ่มตัว

ตัวเร่งปฏิกิริยาปริมาณ 0.2 กรัมถูกบรรจุในเซลล์ทำด้วย quartz และประกอบเข้ากับเตาอบที่ควบคุมอุณหภูมิได้และเชื่อมต่อกับ TCD ก๊าซฮีเลียมถูกป้อนเข้าสู่เซลล์ด้วยอัตราการไหล $30\text{ ml}/\text{min}$ เพื่อกำจัดอากาศที่เหลืออยู่ในเซลล์ ก่อนทำการดูดซับตัวอย่างจะถูกรีดิวซ์ด้วยไฮโดรเจนที่อัตราการไหล $50\text{ ml}/\text{min}$ ที่อุณหภูมิ 500°C เป็นเวลา 2 ชั่วโมง โดยอัตราการเพิ่มอุณหภูมิเท่ากับ $10^{\circ}\text{C}/\text{min}$ หลังจากนั้นตัวอย่างถูกทำให้เย็นจนถึงอุณหภูมิห้องด้วยก๊าซฮีเลียม คาร์บอนมอนอกไซด์ถูกฉีดเข้าสู่เซลล์เป็นจังหวะ คาร์บอนมอนอกไซด์ที่ไม่ถูกดูดซับจะถูกวัดด้วย TCD และจะฉีดคาร์บอนมอนอกไซด์ไปจนกระทั่งไม่มีการดูดซับคาร์บอนมอนอกไซด์เพิ่ม

3.4.3.3 การวิเคราะห์ค่าความเป็นกรดของตัวเร่งปฏิกิริยาด้วยไพรีดิน

เครื่องมือและอุปกรณ์

1. เครื่อง Fourier transform infrared spectroscopy (FT-IR) ใช้เป็นเครื่องตรวจสอบการดูดซับของไพรีดิน ในการทดลองใช้รุ่น Nicolet model Impact 400 FT-IR ซึ่งมีตัวตรวจสอบแบบ deuterated triglycine sulfate (DTGS)
2. เซลล์สำหรับใช้ใส่สารในการทดลอง เซลล์ทำจากควอทซ์และปิดหัวท้ายด้วย KBr ซึ่งมี O-ring เป็นตัวปิดกันอากาศเข้าสู่ระบบ
3. เครื่องมือที่ใช้ในการทดสอบทำจากเครื่องแก้ว มีหลอดทดลองสำหรับบรรจุไพรีดินเหลว หลอดทดลองสำหรับกักเก็บไอของไพรีดิน และมีสูญญากาศ

วิธีการทดลอง

การทดสอบแบ่งออกเป็น 2 ขั้นตอน คือ ขั้นตอนการเตรียมสารตัวอย่าง และ ขั้นตอนการทดสอบ

ขั้นตอนที่ 1: การเตรียมสารตัวอย่าง

นำสารตัวอย่างน้ำหนักประมาณ 0.06 g มาบดให้ละเอียด และขึ้นรูปด้วยแรงอัด $140-180 \text{ kg/cm}^2$ ให้เป็นแผ่นกลมและบาง แผ่นสารตัวอย่างมีความหนาแน่น 15 ถึง 20 mg/cm^2 ถูกบรรจุในเซลล์ ซึ่งนำไปบรรจุในชุดอุปกรณ์ทดลองระบบปิด

ขั้นตอนที่ 2: การทดสอบ

หลังจากบรรจุเซลล์ในชุดอุปกรณ์ทดลอง ทดสอบสัญญาณอินฟราเรดก่อนมีการดูดซับไพรดีน พร้อมกับบันทึกค่าสัญญาณ หลังจากนั้นจะทำระบบให้เป็นสูญญากาศ โดยใช้ปั๊มสูญญากาศดึงอากาศภายในชุดอุปกรณ์ เป็นระยะเวลา 30 นาที ซึ่งไอของไพรดีนในหลอดทดลอง จะกระจายในระบบสูญญากาศ และดูดซับบริเวณพื้นผิวของสารตัวอย่าง ณ ตำแหน่งที่รับอิเล็กตรอน การดูดซับจะใช้เวลาจนกระทั่งพบว่าสัญญาณของไพรดีนไม่เปลี่ยนแปลง เปิดปั๊มสูญญากาศอีกครั้งเพื่อดึงไอของไพรดีนในระบบและไพรดีนที่ดูดซับโดยแรงทางกายภาพจนพบว่าสัญญาณอินฟราเรดไม่เปลี่ยนแปลง ใช้เวลาประมาณ 1.5 ชั่วโมง จากนั้นเริ่มทำการทดสอบโดยเพิ่มอุณหภูมิให้กับระบบครั้งละ 25°C และทดสอบสัญญาณอินฟราเรด จนกระทั่งพบว่าสัญญาณอินฟราเรดของการดูดซับไพรดีนหมดไป จึงหยุดเพิ่มอุณหภูมิ และสิ้นสุดการทดลอง จากการทดลองจะพบอุณหภูมิสูงสุดที่สามารถดึงไพรดีนหลุดออกจากพื้นผิวได้

3.4.3.4 วิเคราะห์ค่าความเป็นกรดของตัวเร่งปฏิกิริยาด้วยแก๊ส NH_3

ความเป็นกรดบนพื้นผิวของตัวเร่งปฏิกิริยานั้นวัดด้วยเทคนิค temperature-programmed desorption โดยใช้ก๊าซแอมโมเนียด้วยเครื่อง Micromeritics Chemisorb 2750 (pulse chemisorption system) ตัวเร่งปฏิกิริยาปริมาณ 0.1 กรัมถูกบรรจุในเซลล์ทำด้วย quartz ตัวอย่างถูกให้ความร้อนที่อุณหภูมิ 450°C ภายใต้การไหลของก๊าซฮีเลียมเป็นเวลา 1 ชั่วโมงเพื่อกำจัดน้ำที่อยู่บนพื้นผิวของตัวเร่งปฏิกิริยา หลังจากตัวอย่างเย็นลงจนถึงอุณหภูมิ 100°C ก๊าซผสมของ 15% แอมโมเนียในฮีเลียมถูกป้อนเข้าสู่เซลล์เพื่อทำให้พื้นผิวอิ่มตัวด้วยแอมโมเนีย ตัวเร่งปฏิกิริยาถูกเป่าด้วยฮีเลียมที่ 100°C เป็นเวลา 1 ชั่วโมงเพื่อกำจัดแอมโมเนียที่ดูดซับทางกายภาพออกไป จากนั้นตัวอย่างถูกให้ความร้อนจนถึงอุณหภูมิ 450°C ด้วยอัตราการเพิ่มอุณหภูมิเท่ากับ 20°C/min ภายใต้การไหลของฮีเลียมที่ 50 ml/min จำนวนตำแหน่งที่เป็นกรดบนพื้นผิวคำนวณได้จากปริมาณก๊าซแอมโมเนียที่คายออกมาที่วัดได้

3.4.3.5 การวิเคราะห์ค่าความเป็นเบสของตัวเร่งปฏิกิริยา

ความเป็นเบสบนพื้นผิวของตัวเร่งปฏิกิริยานั้นวัดด้วยเทคนิค temperature-programmed desorption โดยใช้ก๊าซคาร์บอนไดออกไซด์ด้วยเครื่อง Micromeritics Chemisorb 2750 (pulse chemisorption system) ตัวเร่งปฏิกิริยาปริมาณ 0.1 กรัมถูกบรรจุในเซลล์ทำด้วย quartz ตัวอย่างถูกให้ความร้อนที่อุณหภูมิ 450°C ภายใต้การไหลของก๊าซฮีเลียมเป็นเวลา 1 ชั่วโมงเพื่อกำจัดน้ำที่อยู่บนพื้นผิวของตัวเร่งปฏิกิริยา หลังจากตัวอย่างเย็นลงจนถึงอุณหภูมิ 100°C ก๊าซคาร์บอนไดออกไซด์ถูกป้อนเข้าสู่เซลล์เพื่อทำให้พื้นผิวอิ่มตัวด้วยคาร์บอนไดออกไซด์ ตัวเร่งปฏิกิริยาถูกเป่าด้วยฮีเลียมที่ 100°C เป็นเวลา 1 ชั่วโมงเพื่อกำจัดคาร์บอนไดออกไซด์ที่ดูดซับทางกายภาพออกไป จากนั้นตัวอย่างถูกให้ความร้อนจนถึงอุณหภูมิ 450°C ด้วยอัตราการเพิ่มอุณหภูมิเท่ากับ $20^{\circ}\text{C}/\text{min}$ ภายใต้การไหลของฮีเลียมที่ $50\text{ ml}/\text{min}$ จำนวนตำแหน่งที่เป็นเบสบนพื้นผิวคำนวณได้จากปริมาณก๊าซแอมโมเนียที่คายออกมาที่วัดได้

3.4.3.6 การวิเคราะห์ค่าความสามารถในการรีดิวซ์ของตัวเร่งปฏิกิริยา

ความสามารถในการรีดิวซ์ของตัวเร่งปฏิกิริยานั้นวัดด้วยเทคนิค temperature-programmed reduction โดยใช้ก๊าซไฮโดรเจนด้วยเครื่อง Micromeritics Chemisorb 2750 (pulse chemisorption system) ตัวเร่งปฏิกิริยาปริมาณ 0.1 ถึง 0.2 กรัมถูกบรรจุในเซลล์ทำด้วย quartz ตัวอย่างถูกให้ความร้อนที่อุณหภูมิ 200°C ภายใต้การไหลของก๊าซฮีเลียมที่ $25\text{ ml}/\text{min}$ เป็นเวลา 1 ชั่วโมงเพื่อกำจัดน้ำที่อยู่บนพื้นผิวของตัวเร่งปฏิกิริยา หลังจากตัวอย่างเย็นลงจนถึงอุณหภูมิ 100°C ก๊าซผสมของ 10% ไฮโดรเจนในอาร์กอนถูกป้อนเข้าสู่เซลล์ ตัวเร่งปฏิกิริยาถูกให้ความร้อนจนถึงอุณหภูมิที่ต้องการในช่วง 100 ถึง 800°C ด้วยอัตราการเพิ่มอุณหภูมิเท่ากับ $10^{\circ}\text{C}/\text{min}$ ปริมาณไฮโดรเจนที่ใช้ไปวัดด้วย TCD และนำไปคำนวณหาค่าความสามารถในการรีดิวซ์ของตัวเร่งปฏิกิริยา

3.4.4 การวิเคราะห์ลักษณะของโค้กที่เกิดขึ้นด้วยเทคนิคการออกซิเดชันแบบโปรแกรมอุณหภูมิ

การวิเคราะห์ลักษณะของโค้กที่เกิดขึ้นบนตัวเร่งปฏิกิริยานั้นใช้เทคนิค temperature-programmed oxidation ด้วยเครื่อง Micromeritics Chemisorb 2750 (pulse chemisorption system) ตัวเร่งปฏิกิริยาปริมาณ 0.1 ถึง 0.2 กรัมถูกบรรจุในเซลล์ทำด้วย quartz ตัวอย่างถูกให้ความร้อนที่อุณหภูมิ 200°C ภายใต้การไหลของก๊าซฮีเลียมที่ $25\text{ ml}/\text{min}$ เป็นเวลา 1 ชั่วโมงเพื่อกำจัดน้ำที่อยู่บนพื้นผิวของตัวเร่งปฏิกิริยา หลังจากตัวอย่าง

เย็นลงจนถึงอุณหภูมิ 100°C ก๊าซผสมของ 1% ออกซิเจนในไฮโดรเจนถูกป้อนเข้าสู่เซลล์
ตัวเร่งปฏิกิริยาถูกให้ความร้อนจนถึงอุณหภูมิที่ต้องการในช่วง 100 ถึง 800°C ด้วยอัตรา
การเพิ่มอุณหภูมิเท่ากับ 10°C/min ปริมาณคาร์บอนไดออกไซด์ที่เกิดขึ้นวัดด้วย TCD และ
นำไปหาลักษณะของโค้กที่เกิดขึ้นบนตัวเร่งปฏิกิริยา

4. แผนการดำเนินงานวิจัยในแต่ละช่วง 6 เดือนตลอดระยะเวลาโครงการ

- 4.1 รวบรวมฐานข้อมูลวิจัยที่เกี่ยวข้อง
- 4.2 ดำเนินการวิจัยตามเป้าหมาย
- 4.3 สรุปและผลวิจัย
- 4.4 เขียนบทความวิจัยต่างประเทศ
- 4.5 จัดทำรายงานความก้าวหน้า
- 4.6 จัดทำรายงานประจำปี
- 4.7 จัดเสนอผลงานวิจัยประจำปี

แผนการดำเนินโครงการตลอด 3 ปี

กิจกรรม/ เดือน	1-6	7-12	13-18	19-24	25-30	31-36
4.1						
4.2						
4.3						
4.4						
4.5						
4.6						
4.7						

5. ผลที่คาดว่าจะได้จากโครงการ

5.1 ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ (ปีละ 10 เรื่อง)

5.2 ผลงานการจดสิทธิบัตร

คาดว่าจะมี 1 เรื่อง เมื่อสิ้นสุดโครงการ

5.3 หนังสือ

คาดว่าจะมีหนังสือ 1 เล่ม เมื่อสิ้นสุดโครงการ

5.4 จำนวน นักวิจัยที่สร้างจากโครงการ

จำนวนวิศวกร/นักวิจัยระดับปริญญาโท 35 คน

จำนวนวิศวกร/นักวิจัย ระดับปริญญาเอก 6 คน

5.5 ประโยชน์ที่คาดว่าจะได้รับ

- 1) สามารถมีบทความที่ตีพิมพ์ในวารสารระดับนานาชาติ ได้อย่างน้อย 30 เรื่อง
- 2) สามารถผลิตจำนวนวิศวกร/นักวิจัยระดับปริญญาโท 35 คน
- 3) สามารถผลิตจำนวนวิศวกร/นักวิจัย ระดับปริญญาเอก 6 คน
- 4) เป็นศูนย์กลางในการทดสอบตัวเร่งปฏิกิริยาให้แก่อุตสาหกรรม

6. รายชื่อ สังกัด โทรศัพท์ และ e-mail ของผู้ร่วมวิจัย

- 6.1 หัวหน้าโครงการ ศาสตราจารย์ ดร. ปิยะสาร ประเสริฐธรรม
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
โทร. 02-218-6883; e-mail: piyasan.p@chula.ac.th
- 6.2 ผู้ร่วมวิจัย ผู้ช่วยศาสตราจารย์ ดร. สุพจน์ พัฒนะศรี
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
โทร. 02-218-6890; e-mail: s_phatanasri@yahoo.com
- 6.3 ผู้ร่วมวิจัย รองศาสตราจารย์ ดร. ชราธร มงคลศรี
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โทร. 0-2218-6867; e-mail: Tharathon.m@eng.chula.ac.th
- 6.4 ผู้ร่วมวิจัย ศาสตราจารย์ ดร. สุทธิชัย อัสสะบำรุงรัตน์
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

- โทร. 0-2218-6868; e-mail: Suttichai.A@eng.chula.ac.th
- 6.5 ผู้ร่วมวิจัย รองศาสตราจารย์ ดร. บรรเจิด จงสมจิตร
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
โทร. 0-2218-6869; e-mail: Bunjerd.j@chula.ac.th
- 6.6 ผู้ร่วมวิจัย ดร. อัครวัต ศิริสุข
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
โทร. 0-2218-6863; e-mail: akawat.s@chula.ac.th
- 6.7 ผู้ร่วมวิจัย รองศาสตราจารย์ ดร. จุงใจ ปั้นประนต
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
โทร. 0-2218-6869; e-mail: joonjai.j@chula.ac.th
- 6.8 ผู้ร่วมวิจัย ผู้ช่วยศาสตราจารย์ ดร. ชวงส์ ชัยสุข
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์และเทคโนโลยีอุตสาหกรรม
มหาวิทยาลัยศิลปากร
โทร. 034-219-364; e-mail: gnowoohc@hotmail.com
- 6.9 ผู้ร่วมวิจัย ผู้ช่วยศาสตราจารย์ ดร.โอกร เมฆาสุวรรณคำรง
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์และเทคโนโลยีอุตสาหกรรม
มหาวิทยาลัยศิลปากร
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- 6.10 ผู้ร่วมวิจัย ผู้ช่วยศาสตราจารย์ ดร. ดวงกมล ณ ระนอง
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ สถาบันเทคโนโลยีพระจอม
เกล้าเจ้าคุณทหารลาดกระบัง
โทร. 02-739-2416 ต่อ 169; e-mail: knduangk@kmitl.ac.th
- 6.11 ผู้ร่วมวิจัย ดร. สร้อยพัทธา สร้อยสุวรรณ
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ มหาวิทยาลัยบูรพา
โทร. 038-102-222 ต่อ 3351; e-mail: soipatta@yahoo.com

7. สรุปเนื้อหางานวิจัยและผลที่ได้รับ

ตารางที่ 3 แสดงผลที่คาดว่าจะได้รับจากโครงการวิจัยเทียบกับผลลัพธ์ที่ได้จริง

ลำดับ	ผลที่คาดว่าจะได้รับ	ผลลัพธ์ที่ได้จริง
1	ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ รวมทั้งสิ้น 30 เรื่อง	ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ รวมทั้งสิ้น 32 เรื่อง (เอกสารแนบ 1-32)
2	การจดสิทธิบัตร 1 เรื่อง	ได้ยื่นจดสิทธิบัตร 1 เรื่อง (เอกสารแนบ 33)
3	หนังสือ 1 เรื่อง	หนังสือ 1 เรื่อง ความรู้พื้นฐานของตัวเร่ง ปฏิกิริยาวิวิธพันธุ์ โดย จุงใจ ปิ่นประณต ๒๕๕๔
4	บัณฑิตระดับปริญญาโท 35 คน บัณฑิตระดับปริญญาเอก 6 คน	บัณฑิตระดับปริญญาโท 40 คน* บัณฑิตระดับปริญญาเอก 10 คน**

*รายชื่อบัณฑิตระดับปริญญาโท จบปีการศึกษา 2552-54 จำนวน 40 คน

นาย สมจิตร พุดดี

นาย ญัฐปภัฏ ศรีสวัสดิ์

น.ส.ธมลวรรณ อาจารย์พิพัฒน์

นาย พิธิฐ ภัคดี

นาย วสุ ไชยตรี

น.ส. นภาพร เทียงซัด

น.ส.จิราภรณ์ ปุริวัฒน์

นาย กฤษณ์ เลิศเจียมรัตน์

น.ส.สุพุมล สิงชัย

น.ส.กมลวรรณ จันทรมงคลทิพย์

น.ส.วนิดา ทัพพกิจ

น.ส.พิมพ์ปฎิมา ปาณุปากรณ์

น.ส.ปิยะรัตน์ รอดผล

นายฉัตรชัย ชาราวดี

น.ส.จีรติ อบอวย

นายกิตติพงษ์ ไพรศรี

นายวิทยา เหวรรักษ์
นายวุฒิพงศ์ สุวรรณ
นายปรัชญา วารสิทธิ์
นายรัช อินทร
นส.ชลวรรณ เจษฎานุรักษ์
นายอนิรุทธิ์ เล็กสมบุญ
นายเบญจพล นิธิเจริญวงศ์
นส.อรชิตา เย็นจิตต์รัตนวลี
นส.แพรว รอดกิจ
นายอภิวัฒน์ ไ้วชนะวัฒน์
นายสมชาติ อมรเลิศปรีชา
นายวรวัฒน์ ชื่นชีพ
นายจักรพันธ์ จันละมูล
นายเอกรัตน์ บัวพัน
นายวรวิทย์ ชื่นชีพ
น.ส.มาลี วงศ์เทพ
นายวิทวัส ชูกิจธนสาร
นายจิรวัฒน์ ภิญโญชีพ
น.ส.ศิวนาถ ขุนทอง
น.ส. แพรวพรรณ คั่นชนะเนตร
น.ส. บงกช ปิยานันทรักษ์
น.ส. เกียรติลดา วารินศิริรักษ์
น.ส. สุนันทา แก่นทอง
น.ส. ฤดีมาส มโนศักดิ์

****รายชื่อบัณฑิตระดับปริญญาเอก จบปีการศึกษา 2552-54 จำนวน 10 คน**

น.ส.กานดา ปัทมาคมสัน
นส.พัชราภรณ์ ไกวัลชัชวาล
นายเอกราชชัย ไชยชนะ
น.ส.เพ็ญพิศ วงศ์มณี
น.ส.ณัฐญา คู่มทรัพย์
น.ส.กนกวรรณ จ้าวสุวรรณ

นายธงชัย กลิ่นห้าน

นายนิคม แซ่ม่า

น.ส.ณิชาภัทร เชนโส

น.ส. ศุภนันท์ ปัทมะสังข์

ภาคผนวก A

Reprint บทความวิจัยต่างประเทศ

จำนวน 32 เรื่อง

Research output paper for DPG5280005 (Prof. Piyasan Prasertthdam)

1st year

No	Title	Volume/Page/Year	Journal	IF (2011)	Acknowledgement (in paper)
1	“Modification of acid properties and catalytic properties of AlPO ₄ by hydrothermal pretreatment for methanol dehydration to dimethyl ether” [Krit Lertjiamrath, Piyasan Prasertthdam , Masahiko Arai, Joongjai Panpranot*]	378, 119-123, 2010	Applied Catalysis A: General	3.903	TRF&CHE
2	“Impact of Si and Zr addition on the surface defect and photocatalytic activity of the nanocrystalline TiO ₂ synthesized by the solvothermal method” [Piyawat Supphasirongjaroen, Piyasan Prasertthdam , Okorn Mekasuwandumrong, Joongjai Panpranot*]	36, 1439-1446, 2010	Ceramics International	1.751	TRF&CHE
3	“Effect of Milling on the formation of nanocrystalline χ -Al ₂ O ₃ from Gibbsite” [Wasu Chaitree, Sirithan Jiemsirilers, Okorn Mekasuwandumrong, Piyasan Prasertthdam , Tawatchai Charinpanitkul, Joongjai Panpranot*]	89, 2387-2392, 2010	Journal of the American Ceramic Society	2.272	TRF&CHE
4	“Improvement of propane oxidation activity over Pt/Al ₂ O ₃ by the use of mixed γ - and χ -Al ₂ O ₃ supports” [Thongchai Glinrun, Okorn Mekasuwandumrong, Joongjai Panpranot, Choowong Chaisuk, Piyasan Prasertthdam ,*]	100, 441-448, 2010	Reaction Kinetics Mechanisms and Catalysis	0.927	TRF&CHE

Research output paper for DPG5280005 (Prof. Piyasan Prasertthdam)

No	Title	Volume/Page/Year	Journal	IF (2011)	Acknowledgement (in paper)
5	“Solvent effect on synthesis of zirconia support for tungstated zirconia catalysts” [Peangpit Wongmaneevil, Bunjerd Jongsomjit*, Piyasan Prasertthdam]	16, 327-333, 2010	Journal of Industrial and Engineering Chemistry	1.977	TRF&CHE
6	“The role of zirconia surface on catalytic activity of tungstated zirconia via two-phase esterification of acetic acid and 1-heptanol” [Kanokwan Ngaosuan, Bunjerd Jongsomjit, Piyasan Prasertthdam *,]	136, 134-140, 2010	Catalysis Letters	2.242	TRF&CHE
7	“Ethylene-hexene copolymer derived from [t-butylfluorenylsilyl-amido] dimethyl titanium complex” [Ekrachan Chaichana, Supaporn Khaibunsongserm, Piyasan Prasertthdam , Bunjerd Jongsomjit*]	4, 94-100, 2010	Express Polymer Letters	1.769	TRF&CHE
8	“Study on solvent/alkoxide molar ratios on synthesis zirconia nanoparticles for tungstated zirconia catalysts over esterification” [Peangpit Wongmaneevil, Bunjerd Jongsomjit*, Piyasan Prasertthdam]	139, 42-49, 2010	Catalysis Letters	2.242	TRF&CHE

Research output paper for DPG5280005 (Prof. Piyasan Prasertthdam)

No	Title	Volume/Page/Year	Journal	IF (2011)	Acknowledgement (in paper)
9	“The influence of si-modified TiO ₂ on the activity of Ag/TiO ₂ in CO oxidation” [Nattaya Comsup, Joongjai Panpranot, Piyasan Prasertthdam]	16, 703-707, 2010	Journal of Industrial and Engineering Chemistry	1.977	TRF&CHE
10	“Thermodynamic analysis of calcium oxide assisted hydrogen production from biogas” [S. Assabumrungrat*, P. Sonthisanga, W. Kiatkittipong, N. Laosiripojana, A. Arpornwicheanop, A. Sootitawat, W. Wiyaratn, Piyasan Prasertthdam]	16, 785-789, 2010	Journal of Industrial and Engineering Chemistry	1.977	TRF&CHE

Note: No. 1-10 are the output for 1st year (including in the previous 12-month progress report).

Research output paper for DPG5280005 (Prof. Piyasan Prasertthdam)

2nd Year

No	Title	Volume/Page/Year	Journal	IF (2011)	Acknowledgement (in paper)
11	“Elucidation of the basicity dependence of 1-butene isomerization on MgO/Mg(OH) ₂ catalysts” [Jiraporn Puriwat, Wasu Chaitree, Kongkiat Suriye, Siraprapa Dokjampa, Piyasan Prasertthdam , Joongjai Panpranot [*]]	12, 80-85, 2010	Catalysis Communications	2.986	TRF & CHE
12	“The effect of phosphorous precursor on the CO oxidation activity of P-modified TiO ₂ supported Ag catalysts” [Nattaya Comsup, [*] Joongjai Panpranot, Piyasan Prasertthdam]	11, 1238-1243, 2010	Catalysis Communications	2.986	TRF & CHE
13	“Effects of synthesis conditions and annealing post-treatment on the photocatalytic activities of ZnO nanoparticles in the degradation of methylene blue dye” [Okorn Mekasuwandumrong, Pongspak Pawinrat, Piyasan Prasertthdam , Joongjai Panpranot [*]]	164, 77-84, 2010	Chemical Engineering Journal	3.461	TRF&CHE
14	“Influence of mixed activators on ethylene polymerization and ethylene/1-hexene copolymerization with silica-supported Ziegler-Natta catalyst” [Nichapat Senso, Supaporn Khaubunsongserm, Bunjerd Jongsomjit, Piyasan Prasertthdam [*]]	15, 9323-9339, 2010	Molecules	2.386	TRF&CHE

Research output paper for DPG5280005 (Prof. Piyasan Prasertthdam)

No	Title	Volume/Page/Year	Journal	IF (2011)	Acknowledgement (in paper)
15	“Observation of different catalytic activity of various 1-olefins during ethylene/1-olefin copolymerization with homogeneous metallocene catalysts” [Mingkwan Wannaborworn, Piyasan Prasertthdam , Bunjerd Jongsomjit *]	16, 373-383, 2011	Molecules	2.386	TRF&CHE
16	“Behaviors in ethylene polymerization of $MgCl_2$ - SiO_2 - $TiCl_4$ /THF Ziegler-Natta catalysts with differently treated SiO_2 ” [Nichapat Senso, Bunjerd Jongsomjit, Piyasan Prasertthdam *]	16, 1323-1335, 2011	Molecules	2.386	TRF&CHE
17	“The influence of comonomer on ethylene/ α -olefins copolymers derived from [Bis(N-(3-tert butylsalicylidene) anilinato)] titanium (IV) dichloride complex” [Patcharaporn Kaivalchatchawal, Pattiya Suttititakwong, Sutheerawat Samingprai, Piyasan Prasertthdam , Bunjerd Jongsomjit *]	16, 1655-1666, 2011	Molecules	2.386	TRF&CHE
18	“Effect of Ga modification on different pore size silicas in synthesis of LLDPE by copolymerization of ethylene and 1-hexene with [t-BuNSiMe ₂ Flu]TiMe ₂ /MMAO catalyst” [Ekrachan Chaichana, Supaporn Khaubunsongserm, Piyasan Prasertthdam , Bunjerd Jongsomjit *]	66, 1301-1312, 2011	Polymer Bulletin	1.532	TRF&CHE

Research output paper for DPG5280005 (Prof. Piyasan Prasertthdam)

No	Title	Volume/Page/Year	Journal	IF (2011)	Acknowledgement (in paper)
19	“Flow patterns of liquid multiphase flow in microreactors with different guideline structures” [Chayanoot Kositanont, Sompong Putivisutisak, Piyasan Prasertthdam , Suttichai Assabumrungrat, Hiroshi Yamada, Tomohiko Tagawa*]	44, 649-652, 2011	Journal of Chemical Engineering of Japan	0.662	TRF&CHE
20	“Production of propylene from an unconventional metathesis of ethylene and 2-pentene over $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$ ” [Weena Phongsawat, Benjamas Netivorraksa, Kongkiat Suriye, Siraprapa Dokjampa, Piyasan Prasertthdam , Joongjai Panpranot*]	21, 83-90, 2012	Journal of Natural Gas Chemistry	1.348	TRF&CHE

Note No. 11-20 are the output for 2nd year, including in the previous 24-month progress report.

3rd Year

Research output paper for DPG5280005 (Prof. Piyasan Prasertthdam)

No	Title	Volume/Page/Year	Journal	IF (2011)	Acknowledgement (in paper)
21	“Effect of calcination treatment of zirconia on W/ZrO ₂ catalysts for transesterification” [Nichapat Senso, Bunjerd Jongsomjit*, Piyasan Prasertthdam]	92, 1537-1542, 2011	Fuel Processing Technology	2.945	TRF & CHE
22	“The influence of the t-butyl and cyclododecyl substitution based on ansa-fluorenylamidodimethyltitanium derivatives on ethylene/1-hexene copolymerization” [Patcharaporn Kaivalchatchawal, Piyasan Prasertthdam , Yuuichi Sogo, Zhengguo Cai, Takeshi Shiono, Bunjerd Jongsomjit.]	16, 4122-4130, 2011	Molecules	2.386	TRF & CHE
23	“Effect of Ti oxidation state on ethylene, 1-hexene comonomer polymerization by MgCl ₂ -supported Ziegler-Natta catalysts” [Nichapat Senso, Piyasan Prasertthdam , Bunjerd Jongsomjit, Toshiaki Taniike, Minoru Terano*]	67, 1979-1989, 2011	Polymer Bulletin	1.532	TRF&CHE
24	“Investigation of Ti-Si composite oxide-supported cobalt catalysts over CO ₂ hydrogenation” [Jakrapan Janlamool, Piyasan Prasertthdam , Bunjerd Jongsomjit*]	20, 558-564, 2011	Journal of Natural Gas Chemistry	1.348	TRF&CHE

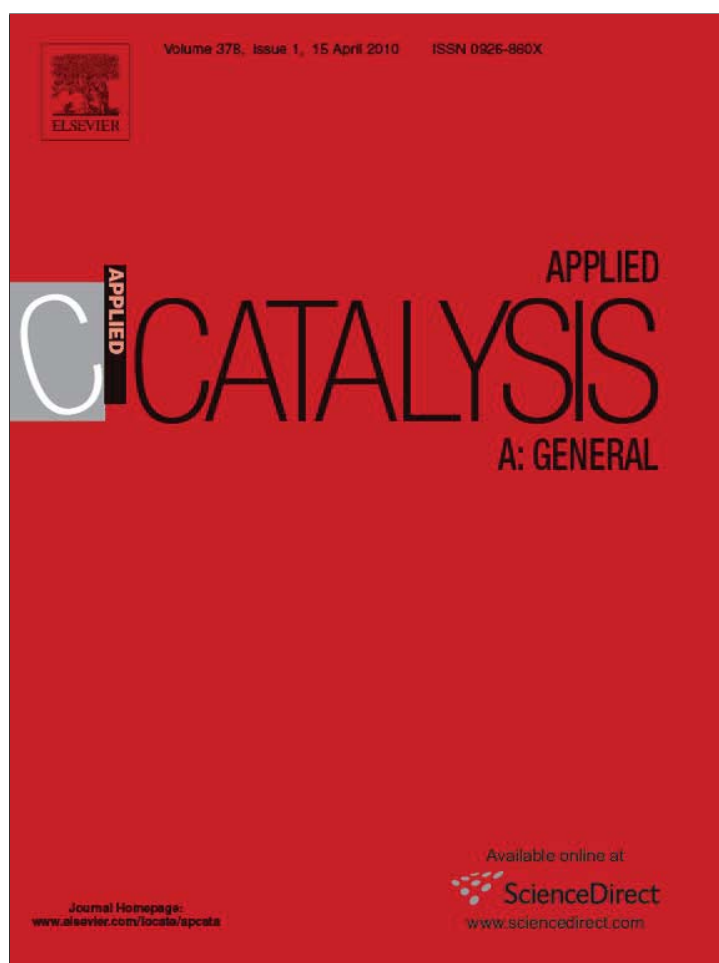
Research output paper for DPG5280005 (Prof. Piyasan Prasertthdam)

No	Title	Volume/Page/Year	Journal	IF (2011)	Acknowledgement (in paper)
25	“LLDPE synthesis via SiO ₂ -Ga-supported zirconocene/MMAO catalyst” [Mingkwana Wannaborworn, Piyasan Prasertthdam , Bunjerd Jongsomjit]	18, 373-377, 2012	Journal of Industrial and Engineering Chemistry	1.977	TRF & CHE
26	“Effect of Ga- and BCl ₃ -modified silica-supported t-BuNSiMe ₂ (2,7-t-Bu ₂ Flu)] TiMe ₂ /MAO catalyst on ethylene/1-hexene copolymerization” [Patcharaporn Kaivalchatchawal, Sutheerawat Samingprai, Takeshi Shiono, Piyasan Prasertthdam , Bunjerd Jongsomjit]	48, 1304-1312, 2012	European Polymer Journal	2.739	TRF & CHE
27	“Role of support nature (γ -Al ₂ O ₃ and SiO ₂ -Al ₂ O ₃) on the performances of rhenium oxide catalysts in the metathesis of ethylene and 2-pentene” [Weena Phongsawat, Benjamas Netiworaksa, Kongkiat Suriye, Siraprapha Dokjampa, Piyasan Prasertthdam , and Joongjai Panpranot]	21, 158-164, 2012	Journal of Natural Gas Chemistry	1.348	TRF & CHE
28	“Effect of SiO ₂ -Al ₂ O ₃ composition on the catalytic performance of the Re ₂ O ₇ catalysts in the metathesis of ethylene and 2-propylene production” [[Weena Phongsawat, Benjamas Netiworaksa, Kongkiat Suriye, Piyasan Prasertthdam , and Joongjai Panpranot*]	142, 1141-1149, 2012	Catalysis Letters	2.242	TRF & CHE
29	“Observation on inhibition of Ti ³⁺ reduction by fumed silica addition in Ziegler-Natta catalyst with in situ ESR” [Jirawat Pinyocheep, Sirachaya Kunjara Na Ayudhya, Bunjerd Jongsomjit*, Piyasan Prasertthdam]	In press, 2012	Journal of Industrial and Engineering Chemistry	1.977	TRF & CHE

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30	“Effect of nanocrystallite size of TiO ₂ on Co/TiO ₂ and Co/TiO ₂ -Ru catalysts over methanation” [Kitima Pinkaew, Piyasan Prasertthdam , Bunjerd Jongsomjit*]	In press, 2012	Korean Journal of Chemical Engineering	0.991	TRF & CHE
31	“Integrated methane decomposition and solid oxide fuel cell for efficient electrical power generation and carbon capture” [Narisra Triphob, Suwimol Wongsakulphasatch, Worapon Kiatkittipong, Tawatchai Charinpanitkul, Piyasan Prasertthdam , Sutichai Assabumrungrat*]	In press, 2012	Chemical Engineering Research & Design	1.968	TRF & CHE
32	“Formation of CoAl ₂ O ₄ nanoparticles via low temperature solid-state reaction of fine gibbsite and cobalt precursor” [Natpakan Srisawad, Wasu Chaitree, Okorn Mekasuwandumrong, Piyasan Prasertthdam , and Joongjai Panpranot*]	Accepted	Journal of Nanomaterials	1.376	TRF & CHE

Note No. 21-32 are the output for 3rd year, including in this present progress report.



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Modification of acid properties and catalytic properties of AlPO_4 by hydrothermal pretreatment for methanol dehydration to dimethyl ether

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ABSTRACT

An amorphous AlPO_4 catalyst prepared by precipitation method was subjected to pretreatment with 10 mol% water vapor at 100–300 °C for 15 min prior to activity tests in the dehydration of methanol to dimethyl ether (DME). The catalysts pretreated at 200–300 °C exhibited higher methanol conversion than the non-treated catalyst while the one treated at a lower temperature of 100 °C showed lower activity. As revealed by FT-IR and FT-Raman results, there was an increase of lattice hydroxyls on the hydrothermally treated catalysts in the form of P-OH group (weak Brønsted acid sites). Amine titration using Hammett indicators confirmed the increase of both strength and number of acid sites on these catalysts. However, hydrothermal pretreatment at 100 °C may result in catalyst poisoning by weakly bonded water molecules instead so that lower catalyst activity was obtained. More than 99% selectivity to DME was achieved on both non-treated and hydrothermally treated AlPO_4 catalysts in this study.

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1. Introduction

Dimethyl ether (DME) is one of the promising alternative fuels that can be used to replace liquefied petroleum gas (LPG) and diesel fuels because of their similar properties to those of LPG and their high cetane number [1–3]. Moreover, DME was identified as the ultraclean alternative fuel for diesel engines with emission levels meeting the California ULEV standards [4]. DME could be produced from either synthesis gas or methanol. The production of DME via methanol dehydration is more favorable as regards thermodynamics and economy [2,5].

Methanol dehydration to DME is usually carried out over solid-acid catalysts such as H-ZSM-5, steam de-aluminated H-Y zeolite (SDY), and $\gamma\text{-Al}_2\text{O}_3$. The most widely used material is probably $\gamma\text{-Al}_2\text{O}_3$, due to its suitable acidity for this reaction that yields good performance in terms of methanol conversion and DME selectivity. Aluminum phosphate (AlPO_4) is also one of the promising catalysts in this reaction, because of its lower amounts of coking and by-products and water resistant property [3,4]. The catalytic activity of AlPO_4 in methanol dehydration was found to be dependent on

the preparation method, chemical composition (Al/P molar ratio), and activation temperature [3,6].

Water may be a poison in methanol dehydration reactions because it could block active sites and impede methanol from adsorption on the catalyst surface [7,8]. Nevertheless, there are a number of studies reporting opposite results. For example, Ludmány et al. [4] have shown that the presence of water in a reaction can increase the catalytic activity of amorphous titanium hydrogen-phosphate ($\text{Ti}(\text{HPO}_4)_2$) in alcohol dehydration due to swollen effect resulting in an increase of the inter layer of $\text{Ti}(\text{HPO}_4)_2$. The swollen catalyst with water and alcohol inside the layers retains its high activity until it loses the alcohol and water by evaporation. Fu et al. [9] also reported a slight increase of activity of SDY zeolite catalyst in methanol dehydration after regeneration under hydrothermal conditions at 500 °C for 2 h. Another hypothesis about why water could increase the activity of alumina-based catalyst is that the Lewis acid sites could change to weak Brønsted acid sites upon contact with humidity [7].

In the present work, an amorphous AlPO_4 catalyst was pretreated under various hydrothermal conditions prior to activity test in the dehydration of methanol. The catalysts were characterized by X-ray diffraction (XRD), N_2 physisorption, Fourier transform infrared spectroscopy (FT-IR), Fourier transform Raman spectroscopy (FT-Raman), and amine titration with Hammett indicators. The catalyst activities were correlated with their surface characteristics and acid properties.

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2. Experimental

2.1. Catalyst preparation

An amorphous AlPO_4 catalyst with Al/P molar ratio = 1 was prepared by a modified version of the aqueous solution precipitation method of Bautista et al. [10]. Firstly, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (analytical grade, Aldrich) was diluted in deionized water and mixed with H_3PO_4 (85%, v/v Aldrich) by stirring at a controlled temperature of 0°C . Then aqueous ammonia solution was added drop-wise until the precipitation occurred at pH of solution ca. 7. The precipitate was filtered out and washed with distilled water to remove excess substances and any contaminants, and then washed again with 2-propanol. The filtrated mass was dried at 110°C overnight and calcined at 650°C in air flow for 3 h.

The AlPO_4 so prepared was subjected to hydrothermal pretreatments at different temperatures. It was exposed to a stream of 10 mol% water vapor in helium at a GHSV $5300\text{ h}^{-1}\text{ cm}^3/\text{min}$ and at temperatures of $100\text{--}300^\circ\text{C}$ for 15 min.

2.2. Catalyst characterization

The XRD patterns of the prepared catalysts were measured from 10° to 80° 2θ using a SIEMENS D5000 X-ray diffractometer and $\text{Cu K}\alpha$ radiation with a Ni filter. Surface area, pore volume, and average pore diameter were measured by N_2 physisorption using a Micromeritics ASAP 2020. FT-IR was performed using a Nicolet 6700 spectrometer in the range of $4000\text{--}400\text{ cm}^{-1}$ at a resolution of 2.0 cm^{-1} . FT-Raman was performed using a PerkinElmer, spectrum GX in the Raman shift range of $200\text{--}3600\text{ cm}^{-1}$ at a resolution of 4.0 cm^{-1} . The acidity of the catalyst samples was determined by amine titration method using Hammett indicators according to Ref. [11]. The NH_3 -TPD was performed in a Micromeritic Chemisorb 2750 automated system. Before adsorption, the sample was pretreated in high purity N_2 ($50\text{ cm}^3/\text{min}$) at 200°C for 1 h. Then, it was saturated with 15% NH_3 -He at 80°C for 1 h ($50\text{ cm}^3/\text{min}$) and subsequently flushed with flowing He at 100°C for 1 h ($50\text{ cm}^3/\text{min}$) to remove physisorbed NH_3 . The temperature-programmed desorption was carried out from 35 to 600°C at a constant heating rate of $10^\circ\text{C}/\text{min}$.

2.3. Catalytic activity test

The dehydration of methanol over non-treated and hydrothermally treated AlPO_4 was carried out in a fixed-bed reactor (i.d. 6 mm) using 0.2 g of catalyst and a gas hourly space velocity (GHSV) of 5300 h^{-1} . Methanol was bubbled by helium through a glass saturator maintained at 29°C . The reaction was conducted at $150\text{--}300^\circ\text{C}$ under atmospheric pressure. The reactant and products were analyzed using a gas chromatograph with a TCD detector and Porapak-Q and Porapak-N columns at 110°C and 100°C , respectively.

3. Results and discussion

3.1. Catalytic activity in the dehydration of methanol

The AlPO_4 synthesized by a modified precipitation method in this work had amorphous structure as determined by XRD (not shown) and possessed a BET surface area of $171.2\text{ m}^2/\text{g}$, a pore volume of $0.758\text{ cm}^3/\text{g}$, and an average pore radius of 17.7 nm. The non-treated AlPO_4 catalyst was tested in the dehydration of methanol to DME at the temperature range $150\text{--}300^\circ\text{C}$ and the results are shown in Fig. 1. As compared to a commercial $\gamma\text{-Al}_2\text{O}_3$ (Aldrich) that possessed BET surface area $149\text{ m}^2/\text{g}$, pore volume $0.23\text{ cm}^3/\text{g}$, and average pore radius 3.7 nm, the catalytic activity

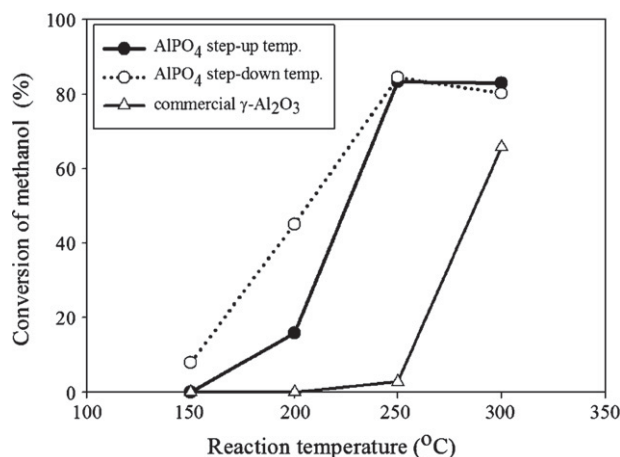


Fig. 1. Methanol conversion profiles of step-up and step-down reaction temperature experiments for the non-treated AlPO_4 catalyst as compared to a commercial $\gamma\text{-Al}_2\text{O}_3$ catalyst (reaction conditions were 0.2 g catalyst, 1 atm, and GHSV = 5300 h^{-1}).

of our synthesized AlPO_4 catalysts in the dehydration of methanol was much higher. Based on the NH_3 -TPD results (Fig. 2), the lower activity of $\gamma\text{-Al}_2\text{O}_3$ was attributed to the lower number of acid sites present. Moreover, while the AlPO_4 catalyst exhibited a large broad peak with the highest peak intensity at ca. 125°C , the commercial $\gamma\text{-Al}_2\text{O}_3$ showed two desorption peaks at ca. 80 and 360°C , indicating the presence of both relatively weak and strong acid sites on $\gamma\text{-Al}_2\text{O}_3$.

The catalytic activities of AlPO_4 catalyst were further investigated in the dehydration of methanol using step-up and step-down reaction temperature tests. For a step-up reaction temperature experiment (increasing temperature from $150 \rightarrow 200 \rightarrow 250 \rightarrow 300^\circ\text{C}$), methanol conversion occurred at 200°C and increased with increasing reaction temperature. Equilibrium conversion ($\sim 82\%$) was reached at 300°C . The AlPO_4 catalyst gave $>99\%$ selectivity to DME with less than 1% of by products such as carbon monoxide and methane. For a step-down reaction temperature experiment using a new catalyst sample (decreasing temperature from $300 \rightarrow 250 \rightarrow 200 \rightarrow 150^\circ\text{C}$), methanol conversion at 200°C increased to 45.1% as compared to 15.3% for the step-up temperature one. The AlPO_4 catalyst also showed some conversion of methanol of ca. 8% at 150°C . It is hypothesized that there was an effect of water vapor and/or initial

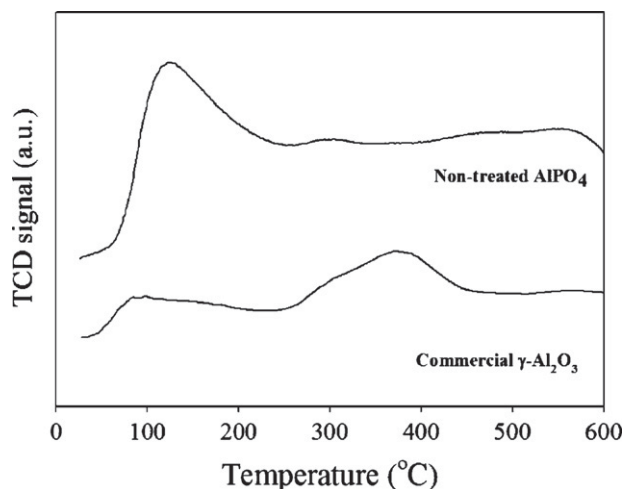


Fig. 2. NH_3 -TPD results of the synthesized- AlPO_4 and the commercial $\gamma\text{-Al}_2\text{O}_3$ catalysts.

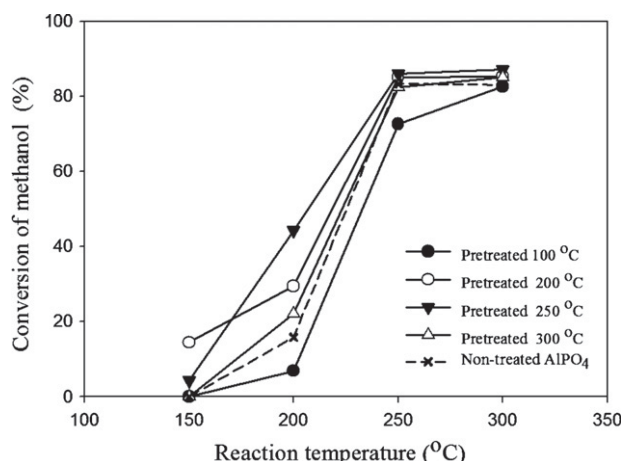


Fig. 3. Effect of water pretreatment temperature on the conversion of methanol for the hydrothermally treated and non-treated amorphous AlPO_4 catalysts (0.2 g catalyst and $\text{GHSV} = 5300 \text{ h}^{-1}$).

high reaction temperature on the improvement of catalytic activity. The latter hypothesis, however, was rejected since treating the AlPO_4 catalyst at 300°C in neutral atmosphere of helium for 1 h prior to reaction test did not result in an increase of catalytic activity (similar conversion to the step-up reaction temperature test). In order to prove the former hypothesis that the presence of water vapor could increase the activity of AlPO_4 in methanol dehydration, we subjected the material to pretreatment with 10 mol% water vapor at various temperatures between 100 – 300°C for 15 min prior to reaction test. The activities of treated and non-treated AlPO_4 catalysts in methanol dehydration are shown in Fig. 3. It was found that all the treated catalysts exhibited higher activity than the non-treated one except the one that was treated at 100°C . There was no change in product selectivity for all the catalysts in which $>99\%$ selectivity to DME was obtained.

3.2. Surface characteristics and acidity of the AlPO_4 catalysts

Surface characteristics and acidity of the catalysts were determined by FT-IR, FT-Raman, and amine titration using Hammett indicators. The AlPO_4 catalysts were investigated by FT-IR in two regions: 400 – 1800 cm^{-1} and 2500 – 4000 cm^{-1} . The results are shown in Figs. 4 and 5, respectively. According to the literature [6,12,13], there are two major types of hydroxyl groups:

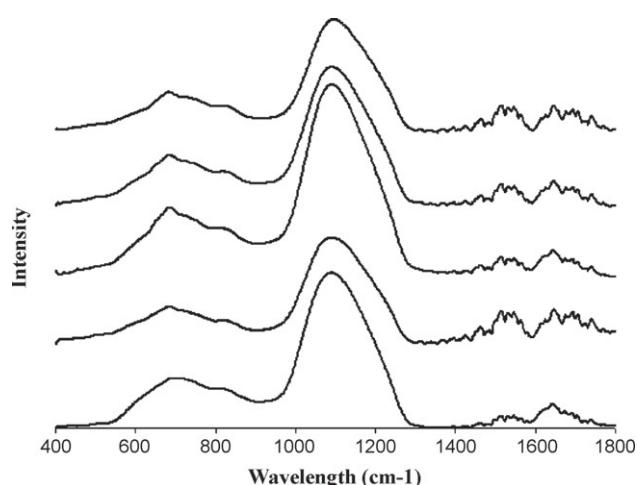


Fig. 4. FTIR spectra at wavelength 400 – 1800 cm^{-1} of the non-treated AlPO_4 and 100 – 300°C water vapor pretreated AlPO_4 catalysts.

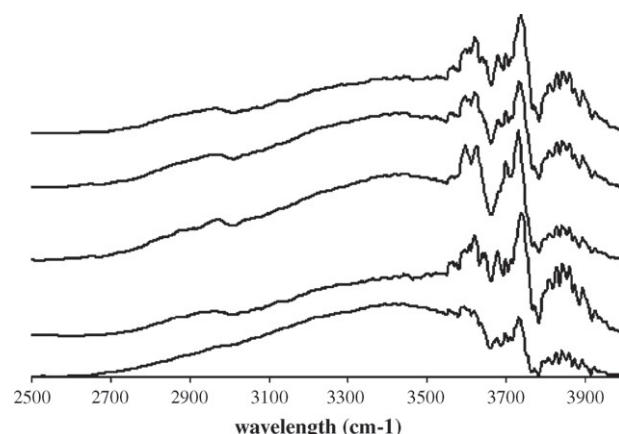


Fig. 5. FTIR spectra at wavelength 2500 – 4000 cm^{-1} of the non-treated AlPO_4 and 100 – 300°C water vapor pretreated AlPO_4 catalysts.

the hydroxyl stretching vibration bands of adsorbed molecular water absorption (surface hydroxyls) and the hydrogen-bonded hydroxyl groups (lattice hydroxyls). In Fig. 3, the peaks in the range around 400 – 800 cm^{-1} were attributed to asymmetric and symmetric stretching vibrations of Al-O-P bonds, corresponding to the non-stoichiometric aluminum phosphates [6]. The peak that centered around 1100 cm^{-1} was attributed to PO_2 in a chain structure with two oxygen atoms from the phosphorous coordination sphere bonded to aluminum atoms [6]. These peaks identifying Al-O-P and PO_2 confirmed that the catalysts were aluminum phosphate. Another peak centered around 1650 cm^{-1} was assigned to the physisorption of water molecules (H-O-H) or surface hydroxyls on the catalysts. There was no significant difference in the water physisorption bands among the non-treated and treated catalyst samples.

The stretching vibration of hydrogen-bonded hydroxyl groups can be detected in the wavelength region of 2500 – 4000 cm^{-1} with a large broad adsorption band centered near 3400 cm^{-1} . These peaks were attributed to the chemisorption of water molecules on the catalyst surface. Using the “fityk 0.7.4” curve fitting program (GNU General Public License, version 2, as published by the free software foundation), we achieved the de-convolution of FT-IR spectra of each catalyst. The results for the non-treated and 250°C -treated AlPO_4 catalysts are shown as examples of the de-convoluted spectra in Fig. 6. The peaks in the region of 2500 – 4000 cm^{-1} for the treated catalysts can be separated into 5 main peaks at 2950 , 3400 , 3600 , 3750 , and 3800 cm^{-1} . There was an absence of an FT-IR peak at 2950 cm^{-1} for the non-treated AlPO_4 catalyst. Moreover, the intensity of FT-IR bands at wavelengths of 3600 and 3750 cm^{-1} of the pretreated AlPO_4 were significantly higher than those of the non-treated one. The strong sharp band around 3750 cm^{-1} accompanied by a broad band around 3400 cm^{-1} could be assigned to the hydroxyl stretching mode of surface phosphate or pyrophosphate species [13]. The shoulder that appeared at ca. 2950 cm^{-1} of the pretreated catalyst suggests the presence of hydroxyl groups of various strengths attached to phosphorous in the samples [6]. These results confirmed that there was an increase of hydroxyls on phosphate groups in the AlPO_4 catalysts after hydrothermal pretreatment. In other words, molecules of water were adsorbed and bonded with phosphorous atoms in the catalysts in the form of P-OH .

The Raman spectra of fresh and pretreated AlPO_4 catalysts are shown in Fig. 7. The Raman bands at 1050 and 1200 cm^{-1} indicate the presence of PO_3^{2-} and PO_2^{1-} , respectively [14]. A study of phosphate groups using Raman spectroscopy by de Jager and Prinsloo [15] showed that Raman shifts around 876 – 992 cm^{-1} could be assigned to P-OH bands in several structures, due to matrix effects

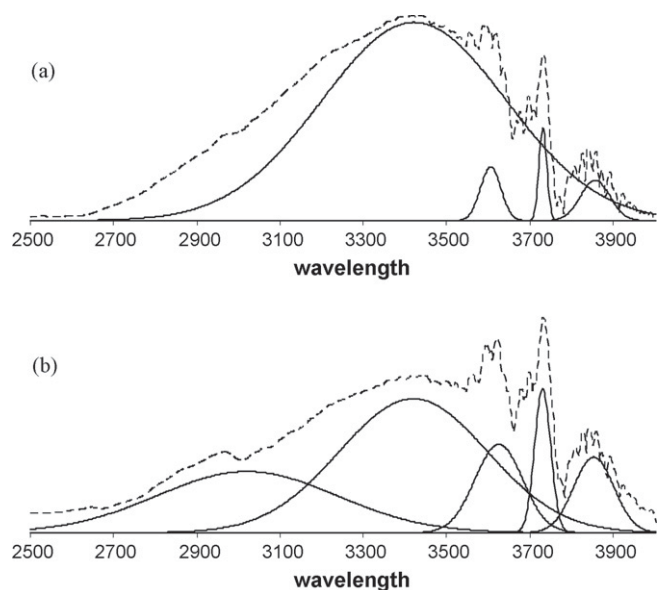


Fig. 6. De-convolution FT-IR spectra of hydroxyl groups of non-treated (a) and 250 °C pretreated (b) AlPO_4 catalysts.

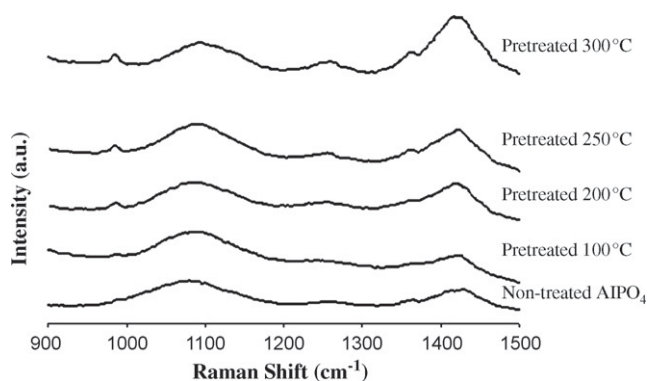


Fig. 7. FT-Raman spectra at Raman shift 900–1500 cm^{-1} of the non-treated AlPO_4 and 100–300 °C water vapor pretreated AlPO_4 catalysts.

and different phosphate functional groups such as PO_2^{1-} , PO_3^{2-} , PO_4^{3-} and $\text{P}_2\text{O}_7^{2-}$. In the present study, the Raman shift at ca. 985 cm^{-1} appeared after pretreatment with water vapor, indicating the formation of P-OH. Such a result was in good agreement with the FT-IR data, which suggested that pretreatment with water vapor could result in the formation of hydroxyls that are adsorbed and chemically bonded with phosphate groups in the AlPO_4 catalyst.

The relative amount of P-OH on the pretreated AlPO_4 catalysts was determined according to the semi-quantitative analysis [16]. For the FT-IR results, it is reported in term of a ratio of the area of de-convoluted hydroxyl peak at 2950 cm^{-1} and the Al-O-P peak

at 833 cm^{-1} . For the FT-Raman results, ratios of the area of P-OH at Raman shift 985 cm^{-1} and PO_2^{1-} at 1200 cm^{-1} were used. The relative amounts of P-OH by semi-quantitative analysis from FT-IR and FT-Raman are shown in Table 1. The highest and the lowest amounts of P-OH were obtained on the AlPO_4 pretreated at 250 and 100 °C, respectively. The amount of P-OH followed the activity trend in the dehydration of methanol to DME.

The strength and number of acid sites of the non-treated and treated AlPO_4 catalysts were also measured by amine titration using Hammett indicators. Values are reported in a range depending on the acid strength (pK_a) of indicators (methyl red, methyl orange, methyl yellow, and crystal violet). The numbers of acid sites in different ranges of Hammett indicators are shown in Table 1. Using methyl red as Hammett indicator, all the treated catalysts changed color to acid form of methyl red while the non-treated catalyst had color in base form. These results indicated that the non-treated AlPO_4 catalyst had lower acid strength than methyl red ($\text{pK}_a = 4.8$). In other words, acidity of the AlPO_4 catalysts after pretreatment with water vapor was higher than $\text{pK}_a = 4.8$. However, all the treated catalysts had color in base form when Hammett indicators with higher acid strength such as methyl orange, methyl yellow, and crystal violet were used so that they could not be titrated by amine. Thus, the acid strength of treated AlPO_4 was in the range of $\text{pK}_a = 4.8$ –3.3, based on the acidity of methyl red and methyl orange, respectively. It was found that the pretreatment with water vapor at 250 °C gave the highest number of acid sites, while the pretreatment at 100 °C resulted in the lowest amount of acidity, in good agreement with results from FT-IR, FT-Raman, and reactions. Since there was no significant change in BET surface area and pore characteristics of the AlPO_4 catalysts upon hydrothermal pretreatment under the conditions used, the differences in the catalytic activities of the hydrothermal treated catalysts could also be attributed to the difference in the distribution of acid strength, in addition to the changes of numbers of acid sites and acid strengths.

3.3. Reaction mechanism

The pretreatment with water vapor at 200–300 °C has been shown to result in an increase of activity of AlPO_4 catalyst in the dehydration of methanol. The improved catalyst performance was attributed to the increase of acid strength and acidity of the AlPO_4 catalyst. As shown by FT-IR and FT-Raman results, there were lattice hydroxyls that are chemically bonded with phosphate groups in the AlPO_4 catalyst after hydrothermal treatment. Such results also suggested a change of Lewis acid sites to Bronsted acid sites on the AlPO_4 catalyst. Higher acid strengths on the pretreated catalysts were confirmed by amine titration using Hammett indicators. According to the mechanism for dehydration of methanol over ZrP and TiP catalysts proposed by Clearfield et al. [17], the P-OH group is involved in water condensation at Bronsted acid sites and formation of methoxy groups on the orthophosphate surface, which are the initial steps for methanol etherification. The methoxy group is

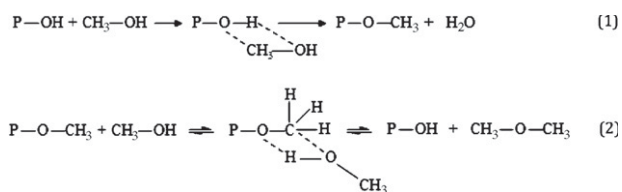
Table 1

The relative amount of P-OH group of hydrothermally treated AlPO_4 samples from FT-IR and FT-Raman calculated by semi-quantitative analysis and the amount of acid sites by amine titration using methyl red indicator.

Pretreatment temperature	Relative amount of P-OH ^a		Amount of acid sites ^b (mmol H ⁺ /g cat.)
	FT-IR at 2950 cm^{-1}	Raman shift at 985 cm^{-1}	
100 °C	0.49	0.00846	0.266
200 °C	1.23	0.02431	0.276
250 °C	1.35	0.03245	0.359
300 °C	0.91	0.02871	0.340

^a See the text for determination.

^b Determined by amine titration using methyl red indicator



Scheme 1. Possible reaction mechanism for dehydration of methanol to DME over AlPO_4 catalyst.

considered to be highly polar due to the strong electronegativity of the phosphate group. The methoxy species can then react with methanol through a four-member ring electron transfer process to form DME. The proposed mechanism is illustrated in Scheme 1. We have clearly shown that P-OH is an important intermediate for the dehydration of methanol over AlPO_4 catalyst.

4. Conclusions

The pretreatment with 10 mol% water vapor at 200–300 °C has been shown to result in an increase of catalytic activity of AlPO_4 catalyst in the dehydration of methanol to DME. The improved catalyst performance was attributed to the increased acid strength and acidity of the AlPO_4 catalyst. The peaks corresponding to P-OH were observed by both FT-IR and FT-Raman techniques. Such results suggested that Lewis acid sites could be changed to Bronsted acid sites on the pretreated AlPO_4 catalysts which would result in higher acid strength, as also confirmed by amine titration with Hammett indicators. However, hydrothermal pretreatment at 100 °C resulted in lower catalytic activity than the non-treated one, due probably to blocking of catalyst active sites by the weakly bonded hydroxyl groups.

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Impact of Si and Zr addition on the surface defect and photocatalytic activity of the nanocrystalline TiO₂ synthesized by the solvothermal method

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Abstract

In the present work, the effects of Si and Zr addition on the surface defect and photocatalytic activity of the solvothermal-derived TiO₂ were investigated. The metal-doped TiO₂ samples were prepared with the molar ratio Si/Ti and Zr/Ti ranging from 0.002 to 0.1 and were subjected to two different cooling temperatures (room temperature and 77 K) after calcination as a post-synthesis treatment. The presence of a small amount of metal dopant caused a slight change in the TiO₂ crystallite and BET surface area (ranging from 7.8 to 10.6 nm and corresponding surface area 95 to 159 m²/g). The photocatalytic activity of TiO₂ did not depend solely on the surface area but rather affected by the concentration of Ti³⁺ on the catalyst surface as shown by a linear ascending trend of the ethylene conversion and the amount of Ti³⁺/surface area of the catalysts. It is noted that addition of Zr had more positive effect than Si and the effect of post-treatment on the photocatalytic activity of TiO₂ catalysts was more pronounced than the addition of metal dopants.

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Keywords: B. Defects; Semiconductor; Nanostructures; Solvothermal; Catalytic properties

1. Introduction

Titanium (IV) dioxide or titania (TiO₂) has a wide range of applications due to its excellent physical and chemical properties. Titania is commercialized as the most powerful photocatalyst because it has high photoactivity for most photocatalytic reactions and is nonexpensive as well as nontoxic to human life [1,2]. The photocatalytic activity of TiO₂ is greatly influenced by its crystal structure, crystallite size, crystallinity, surface area, incident light intensity, and porosity [3]. With the decrease in particle size to nanometer scale, the catalytic activity of titania is enhanced because the optical band gap is widened due to an increase in surface area [4,5], surface defect [6,7], and a shift of the absorption/luminescence spectra towards shorter wavelengths (so-called “blue shift”).

Surface defects in titania crystal are the results of surface oxygen vacancies, which leave Ti³⁺ sites exposed [8,9]. The surface Ti³⁺ sites play an essential role in photocatalytic process over titania photocatalyst [10–12]. Yamazaki et al. [13] reported that the competitive adsorption of water and ethylene molecules occurred on the same Ti⁴⁺ sites while the oxygen molecules adsorbed separately on the Ti³⁺ sites. Thus, an increase of Ti³⁺ sites substantially increased oxygen adsorption and photocatalytic oxidation efficiency. In addition, Park et al. [14] showed that the photoelectrons were trapped by the surface defects (Ti³⁺) leading to the inhibition of the e[−]–h⁺ recombination. Relationship between the amount of Ti³⁺ defects on TiO₂ surface and their photocatalytic activities have been reported by many authors [15–18].

Many methods have been proposed to synthesize nanocrystalline TiO₂ in anatase phase such as sol–gel [19,20], solvothermal [21] and hydrothermal methods [22]. Solvothermal synthesis, in which chemical reactions occur in aqueous or organic media under the self-produced pressure at low temperature (usually lower than 250 °C), is an advantageous

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method because it does not require high temperature treatment step that usually causes grain growth, reduction in specific surface area, and phase transformation of the TiO_2 particles as occurred in the sol–gel process [23]. The solvothermal method has been used to successfully synthesize various types of nanosized metal oxides with large surface area, high crystallinity, and high thermal stability [24,25].

Incorporation of metals into anatase phase TiO_2 has been frequently studied as a way to improve the photocatalytic activity of TiO_2 nanoparticles. Addition of a second metal such as silicon [26,27], zirconium [28], tungsten [29], cerium [30] and aluminium [31] has shown to enhance the thermal stability for phase transformation of titania particles from anatase to rutile and increase the surface area of titania. For example [32], anatase-type TiO_2 doped with 4.7 and 12.4 mol% ZrO_2 that were directly precipitated as nanometer-sized particles from acidic precursor solutions of TiOSO_4 and $\text{Zr}(\text{SO}_4)_2$ by simultaneous hydrolysis under hydrothermal conditions at 200 °C, showed higher photocatalytic activity than pure anatase-type TiO_2 for the decomposition of methylene blue. The thermal stability for phase transition from anatase to rutile of TiO_2 doped with ZrO_2 was greatly improved. Cheng et al. [33] reported that silica-doped TiO_2 showed high photocatalytic activity due to the suppression of phase transformation of titania from anatase to rutile and formation of oxygen vacancies.

However, in most of the aforementioned studies, the effect of second metal addition on the photocatalytic activity of TiO_2 was studied at relatively high metal contents (10–50 wt.%). Thus, it is of interest for this study to investigate the effect of second metal addition (Si and Zr) at relatively low metal content (Si/Ti and Zr/Ti molar ratio between 0.002 and 0.1) on both surface defect and photocatalytic activity of the TiO_2 -based catalysts. The properties of TiO_2 samples were characterized using various analytical methods such as X-ray diffraction (XRD), N_2 physisorption, electron spin resonance spectroscopy (ESR), and X-ray photoelectron spectroscopy (XPS). Photocatalytic activity of the TiO_2 was tested in a gas-phase decomposition of ethylene under UV irradiation.

2. Experimental

2.1. Preparation of nanocrystalline TiO_2

The TiO_2 catalyst was prepared with a procedure reported by Payakgul et al. [34] using titanium (IV) *n*-butoxide (TNB, Aldrich) as a titanium source. The Si- and Zr-doped TiO_2 were prepared by adding a small amount of TEOS (tetraethylorthosilicate, Aldrich) and zirconium (IV) *n*-butoxide (Aldrich) into the solution of 25 g TNB (Aldrich) in 100 ml toluene, respectively. The molar ratios of Si/Ti and Zr/Ti calculated were in the range 0.002–0.1. Then, set up the test tube in a 300 cm³ autoclave. The gap between the test tube and the autoclave wall was filled with 30 cm³ of the same solvent used in the test tube. The autoclave was purged completely by nitrogen before heating up to the desired temperature, in the range of 573 K at a rate of 2.5 K/min. Autogenously pressure during the reaction gradually increased as the temperature was

raised. Once the prescribed temperature was reached, the temperature was held constant for 2 h. After the system was cooled down, the resulting powders were repeatedly washed with methanol and dried in air.

2.2. Quenching treatment

The detailed experiment has already been reported in our earlier works [35,36]. Prior to quenching, the synthesized catalysts were calcined in air atmosphere at 573 K with a heating rate of 10 K/min for 1 h, and then it was taken out and immediately quenched in air at room temperature and 77 K. After the samples were quenched, all the catalyst samples were dried in air at room temperature and stored in a desiccator.

2.3. Sample nomenclature

The base samples were TiO_2 -RT and TiO_2 -77 K which referred to the TiO_2 catalysts without a second metal addition that were cooled down in air at room temperature (RT) and 77 K after calcination, respectively. The nomenclature used for the metal-doped TiO_2 , for example “0.002-(Si)- TiO_2 -RT” was referred to the Si-doped TiO_2 with Si/Ti molar ratio 0.002 that was cooled down in air at room temperature.

2.4. Characterization

Phase identification and crystallite size of pure and modified nanocrystalline titania were investigated by X-ray diffraction (SIEMENS D5000) using Ni filter Cu K_α radiation from 20° to 80° 2θ . The crystallite size of TiO_2 was determined from half-height width of the 1 0 1 diffraction peak of anatase using the Scherrer equation. The BET surface area was obtained from the N_2 adsorption isotherms measured at 77 K in a Micromeritics ASAP 2000. Electron spin resonance spectroscopy (ESR) was conducted in vacuum at room temperature and without illumination using a JEOL, JES-RE2X electron spin resonance spectrometer. To obtain the “g” value, MnSO_4 was used as reference standard material. The intensity of ESR was calculated using a computer software program ES-PRIT ESR DATA SYSTEM (version 1.6). The XPS measurement was carried out using an AMICUS photoelectron spectrometer equipped with an Mg K_α X-ray as a primary excitation and KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at a pass energy of 75 kV. The background pressure during the spectra accumulation was typically 10^{-6} Pa. Detailed spectral scans were taken over Ti 2p, O 1s, Zr 3d, Si 2p and C 1s regions. All the binding energies were referenced to the C 1s peak at 285.0 eV of the surface adventitious carbon.

2.5. Photocatalytic activity measurement

In photocatalytic experiments, the catalysts were packed into a 60 cm long 9 mm diameter horizontal quartz fixed bed reactor. The weights of the catalysts were kept constant at 0.40 g, and in all cases the illuminated length of catalyst was identical. High purity grade air containing 0.1 vol.% ethylene was continuously

fed at a constant flow rate with a gas hourly space velocity (GHSV) of 120 h^{-1} . An air stream with 0.1 vol.% ethylene was first passed through the reactor without irradiation until reaching gas–solid adsorption equilibrium. Then, UV light ($\lambda = 365 \text{ nm}$) was irradiated on the surface of the catalyst using 125 W mercury lamp (Philips, HPLN). The distance between the lamp and the reactor was 20 cm. The light irradiance at surface of the reactor was 0.65 mW/cm^2 . The irradiated sample area was approximately 4 cm^2 . Analysis of the ethylene feed and other hydrocarbon products were conducted with an on-line SHIMADZU GC-14B gas chromatograph equipped with a flame ionization detector (FID) and VZ-10 column. The retention time of ethylene was approximately around 30 s. Other degradation products such as CO and CO_2 were detected using SHIMADZU GC-8A gas chromatograph equipped with a thermal conductivity detector (TCD) equipped with Molecular sieve 5A and Poropak-Q columns, respectively. Steady state was achieved within ca. 3 h after illumination.

3. Results and discussion

3.1. Textural properties of the TiO_2 photocatalysts

X-ray diffraction patterns of the base TiO_2 and the metal-doped TiO_2 samples with metal/titanium molar ratio 0.1 are shown in Fig. 1. All the samples exhibited the XRD patterns of only pure anatase phase TiO_2 without any contamination of other phases. However, the peak intensities of anatase TiO_2 decreased with the insertion of second metal due probably to the formation of amorphous phases [37]. No diffraction lines of zirconia or silica were observed due to the very small amount and/or the small crystallite sizes of the dopant phase lower than XRD detection limit. Incorporation of Zr and Si into anatase TiO_2 structure has been reported by others [38,39]. The average crystallite sizes of TiO_2 samples were determined from the full

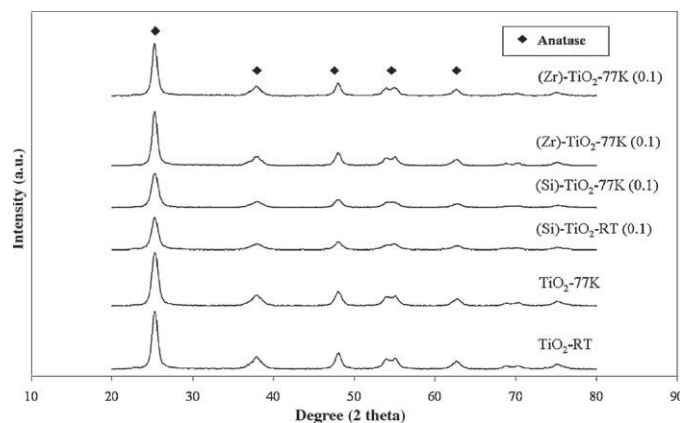


Fig. 1. X-ray diffraction patterns of pure TiO_2 and metal-doped TiO_2 .

width at half maximum of the XRD peak at $2\theta = 25^\circ$ using Scherrer's equation. As shown in Table 1, addition of a small amount of Si or Zr to TiO_2 powder, the average crystallite size of TiO_2 decreased slightly from 11.0 to 9.0 nm. It is likely that second metal doping suppressed crystal growth of TiO_2 thus smaller crystallite sizes were obtained. According to the BET analysis, it can be observed that the Si- and Zr-doped TiO_2 samples have larger BET surface area than pure TiO_2 . The effect was more pronounced for the Si-doped than the Zr-doped ones. The increase in BET surface area can be related with the lower degree of crystallisation of the mixed oxides with respect to the pure TiO_2 . According to Daturi et al. [40], a maximum increase of BET surface area for Zr-modified TiO_2 was observed at the 0.5:0.5 atomic ratio. Thus, we can probably say that addition of relatively small amount of dopant (atomic ratio ≤ 0.1) in this study did not have much impact on the BET surface area of TiO_2 powders. The BET equivalent particle diameters were also calculated and summarized in Table 1. The BET equivalent particle diameters were found to be larger than

Table 1

Physical properties and activities of Si- and Zr-doped TiO_2 samples synthesized by solvothermal method.

Sample nomenclature	BET surface area ^a (m^2/g)	d_{XRD} ^b (nm)	d_{BET} ^c (nm)	Intensity of ESR/BET	Ethylene conversion ^d (%)	TON ^e
TiO_2 -RT	93	10.6	16.8	47	21.5	3.6
TiO_2 -77 K	97	10.6	16.1	257	34.6	5.6
(Si)- TiO_2 -RT (0.002)	159	9.0	9.8	77	23.5	2.3
(Si)- TiO_2 -77 K (0.002)	156	9.0	10.0	199	31.5	3.2
(Si)- TiO_2 -RT (0.005)	133	8.9	11.7	144	27.9	3.3
(Si)- TiO_2 -77 K (0.005)	136	8.6	11.5	213	32.4	3.7
(Si)- TiO_2 -RT (0.1)	133	9.0	11.7	56	22.1	2.6
(Si)- TiO_2 -77 K (0.1)	136	8.4	11.5	62	22.5	2.6
(Zr)- TiO_2 -RT (0.002)	95	9.5	16.4	111	25.7	4.2
(Zr)- TiO_2 -77 K (0.002)	99	9.7	15.8	225	33.2	5.2
(Zr)- TiO_2 -RT (0.005)	101	7.7	15.5	245	34.5	5.3
(Zr)- TiO_2 -77 K (0.005)	106	7.8	14.7	322	39.5	5.8
(Zr)- TiO_2 -RT (0.1)	104	8.2	15.0	57	22.2	3.3
(Zr)- TiO_2 -77 K (0.1)	105	8.4	14.9	79	23.5	3.5

^a Determined using BET method.

^b Determined using Scherrer's equation.

^c Calculated from $d_{\text{BET}} = 6/(\text{SSA} \times \rho_p)$, where ρ_p is the weighted density of TiO_2 (3840 kg/m^3).

^d Photocatalytic reaction was carried out at 313–328 K, 1 bar, and 0.1% ethylene in air.

^e Turnover number.

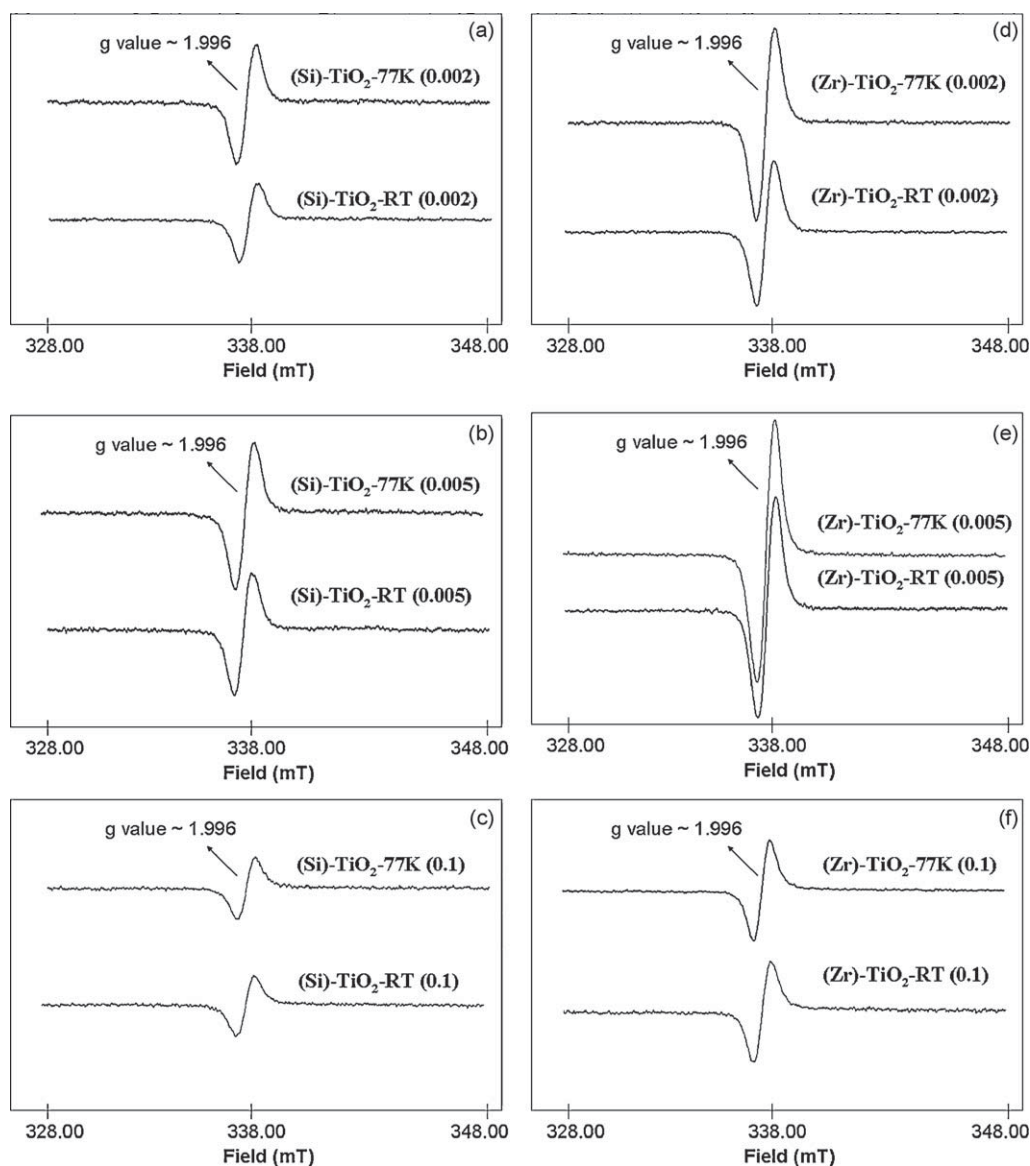


Fig. 2. ESR spectra of (a) 0.002 Si-doped TiO_2 , (b) 0.005 Si-doped TiO_2 , (c) 0.1 Si-doped TiO_2 , (d) 0.002 Zr-doped TiO_2 , (e) 0.005 Zr-doped TiO_2 , and (f) 0.1 Zr-doped TiO_2 .

the ones calculated from XRD results. This can be explained by the agglomeration of TiO_2 particles, which could inhibit the adsorption of N_2 molecules.

It is believed that the process of annealing or calcination has shown to result in a variety of surface defects, strains, and reconstructions of materials [41]. So, the variation of cooling temperature was applied as a post-synthesis treatment with the aim to create more defects on the TiO_2 surface and as a consequence, improve their photocatalytic activities. Moreover, the post-synthesis treatment in cooling temperature did not significantly alter the specific surface area and the average crystallite size of the TiO_2 (see Table 1).

3.2. Electron spin resonance spectroscopy (ESR) study

The number of defective sites of TiO_2 or Ti^{3+} was determined using electron spin resonance spectroscopy

technique and the results are shown in Fig. 2. Nakamura et al. [42] and Serwicka [43] reported two signals occurring on the surface of TiO_2 during ESR analysis without illumination indicating: (i) the surface Ti^{3+} and (ii) the bulk defect. Nakaoka and Nosaka [44] reported six signals in ESR measurement on the surface of titania namely (i) $\text{Ti}^{4+}\text{OH}^-$, (ii) surface Ti^{3+} , (iii) adsorbed oxygen (O^{2-}), (iv) $\text{Ti}^{4+}\text{O}^{2-}$, (v) inner Ti^{3+} , and (vi) adsorbed water. In the present study, all the TiO_2 samples exhibited similar ESR spectra, in which mainly one signal at the g value of 1.996 was observed. According to Nakaoka et al. [42], this peak was attributed to the Ti^{3+} sites on surface TiO_2 . It is clearly seen that the Zr-doped TiO_2 exhibited higher intensity of the ESR signals than the Si-doped ones. The intensity of ESR spectra per surface area of the TiO_2 is given in Table 1. The results indicate that Zr-doped TiO_2 possessed higher concentration of Ti^{3+} defective sites than Si-doped TiO_2 .

Table 2
XPS binding energies (eV) and FWHM (eV) values of Si- and Zr-doped TiO₂ catalysts.

Sample nomenclature	Ti 2p		O 1s		Zr 3d		Si 2p	
	BE	FWHM	BE	FWHM	BE	FWHM	BE	FWHM
TiO ₂ -RT	459.3	1.7	530.8	1.5	–	–	–	–
TiO ₂ -77 K	459.2	1.7	530.6	1.4	–	–	–	–
(Si)-TiO ₂ -RT (0.002)	458.8	1.4	530.1	1.5	–	–	102.1	2
(Si)-TiO ₂ -77 K (0.002)	458.9	1.4	530.2	1.5	–	–	102	1.9
(Si)-TiO ₂ -RT (0.005)	458.3	1.4	530.1	1.5	–	–	102.1	2.1
(Si)-TiO ₂ -77 K (0.005)	458.4	1.4	530.2	1.5	–	–	102.1	2.3
(Si)-TiO ₂ -RT (0.1)	458.5	1.5	530.2	1.6	–	–	102.3	2.2
(Si)-TiO ₂ -77 K (0.1)	458.6	1.5	530.3	1.6	–	–	102.4	2.1
(Zr)-TiO ₂ -RT (0.002)	458.5	1.4	530.2	1.5	182.1	1.8	–	–
(Zr)-TiO ₂ -77 K (0.002)	458.3	1.4	530.1	1.6	182	2	–	–
(Zr)-TiO ₂ -RT (0.005)	458.3	1.5	530.3	1.4	182.1	1.9	–	–
(Zr)-TiO ₂ -77 K (0.005)	458.6	1.4	530.3	1.6	182.4	1.8	–	–
(Zr)-TiO ₂ -RT (0.1)	458.2	1.4	530.1	1.5	182.3	2.2	–	–
(Zr)-TiO ₂ -77 K (0.1)	458.4	1.4	530.3	1.5	182.1	2.1	–	–

3.3. X-ray photoelectron spectroscopy (XPS) study

It is well known that XPS is a surface probe detecting electrons that are generated from a depth of a few nanometers on the surface of the sample. To make the XPS results comparable to those of ESR measurement, elemental composition and chemical states on the surface of metal-doped TiO₂ samples that were subjected to two different cooling temperatures were studied. The binding energy values and the full width at half maximum (FWHM) values of Zr 3d, O 1s, Si 2p and Ti 2p photoelectron peaks as determined by XPS of the various TiO₂ samples are summarized in Table 2. The binding energies for Si 2p and Zr 3d levels are in agreement with those reported for pure SiO₂ [45] and ZrO₂ [46] at 103.0 and 183.5 eV, respectively. No significant variation has been observed for these elements over the metal-doped TiO₂ samples. However, the binding energy of the Ti 2p band for the metal-doped samples was found to be lower than that of the pure TiO₂. For better comparison, the XPS bands of Ti 2p for Si- and Zr-doped TiO₂ are shown in Fig. 3. Normally, the Ti 2p XPS spectra of TiO₂ sample show two shoulder peaks at lower binding energy (Ti 2p_{3/2}) and higher binding energy (Ti 2p_{1/2}), respectively, in line with the earlier reports by Mukhopadhyay

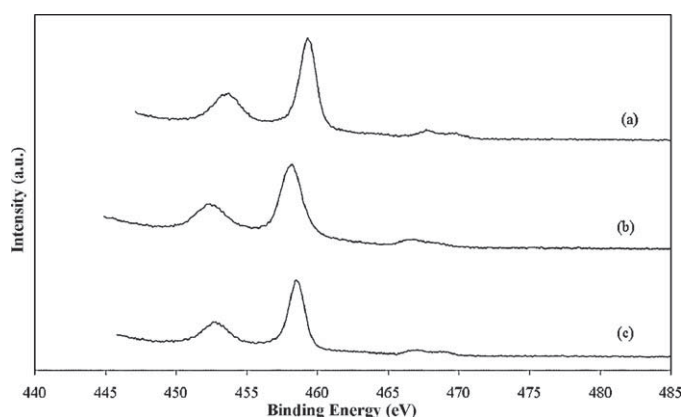


Fig. 3. Ti 2p XPS spectra of various TiO₂ samples: (a) TiO₂-RT, (b) 0.1-(Zr)-TiO₂-RT, and (c) 0.1-(Si)-TiO₂-RT.

and Garofalini [47]. The presence of defect is visible as a shoulder in the XPS spectra which was assigned to Ti³⁺ oxidation state. From Fig. 3, the binding energy of Ti 2p electrons was found to be lower than the value normally published for Ti⁴⁺ ions in TiO₂ (459.2 eV) [48,49]. However, the Ti 2p spectrum was slightly broadened and a shoulder band appeared at 1.6 eV lower than the Ti⁴⁺ binding energy, this could be associated with the Ti³⁺ defect state [50].

3.4. Photocatalytic activity test

The photocatalytic activity of the TiO₂ and metal-doped TiO₂ samples was tested for the photocatalytic decomposition of ethylene in gas-phase under UV illumination. Under these conditions, the only products detected by gas chromatography were CO₂ and H₂O. The mechanism of photocatalytic decomposition of ethylene has been reported by many researchers [13,51]. The mechanism is believed to involve absorption of an UV photo by TiO₂ to produce an electron–hole pair. Both hole and electron play an important role on creating the reaction intermediate, which react further and form CO₂ as the final product.

Photocatalytic activities of the TiO₂ samples with different proportions of Si/Ti and Zr/Ti were evaluated in the decomposition of ethylene in gas-phase and the results are shown in Table 1. In our previous studies [35,36], the effects of cooling media and temperature on the photocatalytic activities of solvothermal-derived TiO₂ have been reported. It was found in this study that the photocatalytic activity of the metal-doped TiO₂ cooled down in different cooling temperatures is also evidently different. The ethylene conversion results show that the metal-doped TiO₂ at lower amounts of metal exhibited higher photocatalytic activity than the pure titania. Ethylene conversions at steady state for the metal-doped TiO₂ samples after cooling at room temperature were ranging from ca. 22% to 39% while pure TiO₂ sample under similar reaction conditions gave ca. 21% ethylene conversion. The turnover number (TON) was calculated from the ratio of the number of photoinduced transformation for a given period of time and the number of

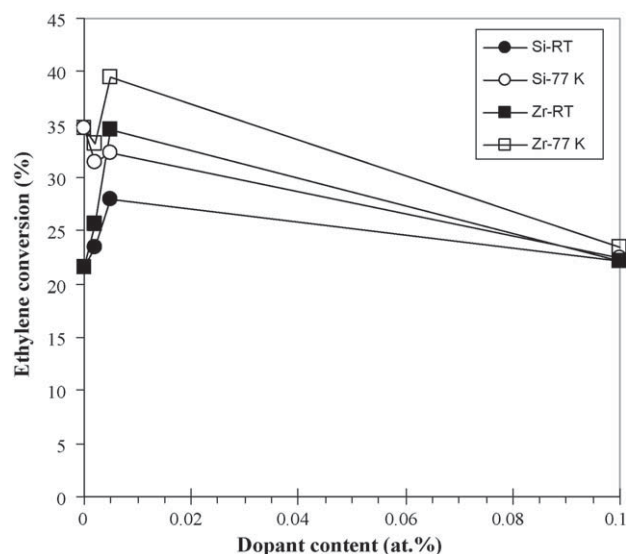


Fig. 4. Plot between ethylene conversion at steady state (ca. 3 h) and dopant content.

photocatalytic sites (surface area). From Table 1, TONs for all the catalysts were greater than unity, the (photo) catalytic character of the reaction or process was confirmed.

The photocatalytic activity of metal-doped TiO_2 depended on the cooling temperature applied after calcination. It was found that metal-doped TiO_2 samples cooled at lower temperature exhibited higher photocatalytic activity than those cooled in high temperature ones. For example, the ethylene conversion of 0.005 Zr-doped TiO_2 was 34.5% and 39.5% for the sample cooled down at room temperature and at 77 K, respectively. Additionally, the metal content has an obvious effect on the activity of the metal-modified TiO_2 catalysts. The plots of ethylene conversion versus metal content (Fig. 4) show that there existed an optimal metal content (atomic ratio) to achieve the highest photocatalytic activity. If the concentration of metal is too low, the promotional effect is not significant while for high metal content, the active sites of TiO_2 may be blocked and lower catalytic activity would be obtained. An optimum metal content on photocatalytic activity of the Zr- and Si-doped TiO_2 has also been suggested by Fu et al. [28] for much higher metal loading range. The specific activity of TiO_2 synthesized by sol–gel method was enhanced by the addition of SiO_2 (optimum at 16 wt.%) or ZrO_2 (optimum at 12 wt.%). The increase in activity of the modified catalysts was attributed to both an increase in surface area (ranging between 250 and 400 m^2/g) and chemical change on the catalyst surface.

The results in this study show that for a similar metal content, the Zr-doped TiO_2 exhibited higher photocatalytic activity than the Si-doped ones. However, one may notice that the Si-doped TiO_2 had larger BET surface areas than the Zr-doped ones and in general, anatase TiO_2 nanoparticles with higher specific surface area typically exhibit higher photocatalytic activity. The increase of surface area means the increase of the number of active sites on which the electron acceptor and donor are adsorbed and participate in the photocatalytic reaction. In our present study, the presence of

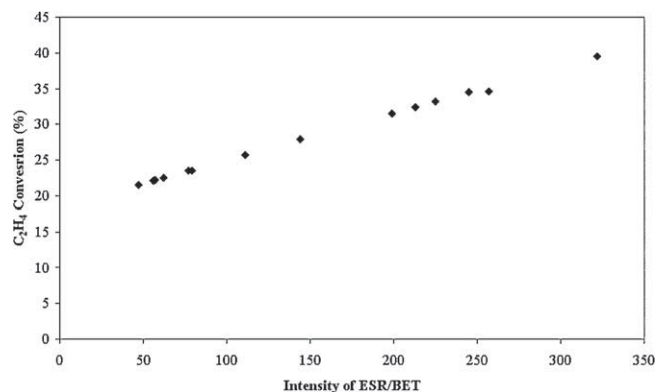


Fig. 5. Photocatalytic activity at steady state (ca. 3 h) of metal-doped TiO_2 for ethylene decomposition as a function of the intensity of ESR/BET.

very small amount of metal dopants caused only a slight change in the TiO_2 crystallite and BET surface area (ranging from 7.8 to 10.6 nm and corresponding surface area 95 to 159 m^2/g). The photocatalytic activity of TiO_2 did not depend solely on the surface area but were found to be correlated well with the concentration of Ti^{3+} on the catalyst surface as illustrated by a linear ascending trend of the ethylene conversion and the amount of Ti^{3+} /surface area of the catalysts in Fig. 5. It should also be noted that the effect of post-treatment on enhancing the concentration of Ti^{3+} on the TiO_2 was more pronounced than the addition of metal dopants.

4. Conclusions

The Si- and Zr-doped TiO_2 with Si/Ti and Zr/Ti molar ratios ranging from 0.002% to 0.1% were prepared via the solvothermal method using titanium *n*-butoxide as the titanium precursor and toluene as the solvent. It was found that selection of a suitable second metal doping can enhance photocatalytic activity of the TiO_2 . Based on ESR and XPS analyses, the improved photocatalytic activity of the TiO_2 is suggested to be due to the presence of Ti^{3+} defect sites on the surface of TiO_2 . Moreover, a post-synthesis treatment by cooling in air at 77 K effectively enhanced the amount of Ti^{3+} and photocatalytic activity of the TiO_2 and the metal-doped TiO_2 .

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Effect of Milling on the Formation of Nanocrystalline χ -Al₂O₃ from Gibbsite

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Gibbsite (FG) with mean particle diameter ($d_{50} = 13 \mu\text{m}$) was milled in an attrition mill for 12 and 24 h using alumina balls as grinding media and calcined at different temperatures in the range of 350–600°C. The properties of the alumina obtained were determined by X-ray diffraction, N₂ physisorption, thermogravimetric/differential thermal analyses, and transmission electron microscopy. Without milling, the alumina obtained normally contained the mixed phases between γ - and χ -phase alumina. On the other hand, high purity of nanocrystalline χ -phase alumina (100 wt%) can be produced by calcination of the 24-h milled FG at 600°C. The isothermal kinetics measurements revealed that the rate constant (k) for phase transformation increased as the particle size of gibbsite decreased and the calculated activation energy for transformation from FG to alumina decreased from 20.6 to 14.7 and 6.8 kJ/mol after milling for 12 and 24 h, respectively. The physical properties of nanocrystalline χ -alumina obtained by the calcination of milled FG were comparable to those produced by the solvothermal method. The present results offer a simple way to prepare a large amount of pure χ -phase alumina for particular industrial applications.

I. Introduction

ALUMINA (Al₂O₃) is one of the most common crystalline materials used as catalysts, catalyst supports, sorbent, coating, and ceramics.^{1–4} Compared with the other oxides, alumina has high surface area, good catalytic activity, high mechanical resistance, good thermal stability, high strength, and toughness.^{5–7} There are many methods to synthesize alumina such as solvothermal,^{5–7} molten salt synthesis,⁸ shock wave action,⁹ sol-gel,¹⁰ spray pyrolysis,¹¹ and thermal decomposition of aluminum hydroxide (boehmite and gibbsite).^{12,13}

χ -alumina is a crystallographic form of series of alumina, which is normally obtained by dehydration of gibbsite (<200 nm).¹⁴ When it is fired, χ -alumina will transform to κ -alumina at a temperature in the range of 650–750°C and consequently form α -alumina at a temperature around 1000°C. The χ -phase alumina has been used as catalysts and catalyst supports and interesting results were obtained.^{15–17} For examples, CO hydrogenation activities of Co/Al₂O₃ catalysts increased when the catalysts were prepared on the mixed γ - and χ -phase Al₂O₃.¹⁵ Khom-in *et al.*¹⁶ studied the solvothermal-derived nanocrystal-

line pure γ -Al₂O₃, χ -Al₂O₃, and mixed-phase γ - and χ -Al₂O₃ in the dehydration reaction of methanol to dimethyl ether. Meephoka *et al.*¹⁷ used both γ - and χ -Al₂O₃ as supports for the preparation of Pt/Al₂O₃ for CO oxidation reaction. Most of the recent studies show that highly stable nanocrystalline χ -Al₂O₃ can be prepared by the solvothermal method using aluminum iso-propoxide as the precursor. Such a technique, however, is quite tedious and costly because it requires a high-pressure reactor, high temperature, and long reaction time.

Gibbsite (α -Al(OH)₃) is a cheap starting material widely used in the transformation of alumina because it can be dehydrated to various phases (χ , γ , θ , κ , α).^{18,19} Figure 1 shows the diagram of phase transformation of alumina from gibbsite. The transformation route depended on temperature, heating environment, particle size of starting gibbsite, and heating rate.²⁰ Typically, for small particles (<1 μm), the phase transformation process occurs by route 1 and produces χ -alumina.¹⁴ In addition, the transformation of bayerite²¹ and diasporite²² to α -Al₂O₃ has been studied. It was indicated that χ -alumina was not formed from these starting materials.

The formation of χ -alumina from gibbsite has been observed in previous works. Jang *et al.*¹² studied the effect of grinding on the phase transformation of gibbsite (starting particle size 64.2 μm). The χ -phase alumina was observed at 450°C for the sample grind for 5 h (particle size 9.7 μm) and completed at around 910°C. Bhattacharya *et al.*²⁰ investigated the thermal decomposition of fine gibbsite (1.5 μm) and the formation of χ -alumina appeared at 500°C and its crystal remained until around 800°C. Mercury *et al.*²³ studied the decomposition of synthetic gibbsite by neutron thermodiffraction and found that χ -alumina was formed at the temperature above 500°C. The grinding method is an effective method for the reduction of particle size due to its simplicity, minimal environmental problems, convenient operation, and absence of wastes. Attrition mills are widely used in order to reduce particle size; moreover, they are ideally appropriate for the industrial process due to their high efficiency and availability in large scale.²⁴

In the present study, the effect of milling on the phase transformation behavior of gibbsite was extensively investigated. The properties of the alumina obtained were investigated using a laser diffraction-based size analyzer, X-ray diffraction (XRD), thermogravimetric/differential thermal analyses (TGA/DTA), N₂ physisorption, transmission electron microscopy (TEM), and isothermal kinetics measurement.

II. Experimental Procedure

(1) Sample Preparation

Gibbsite with $d_{50} = 13.0 \mu\text{m}$ (Merck, Darmstadt, Germany) was used as a starting material. In order to reduce its particle size,

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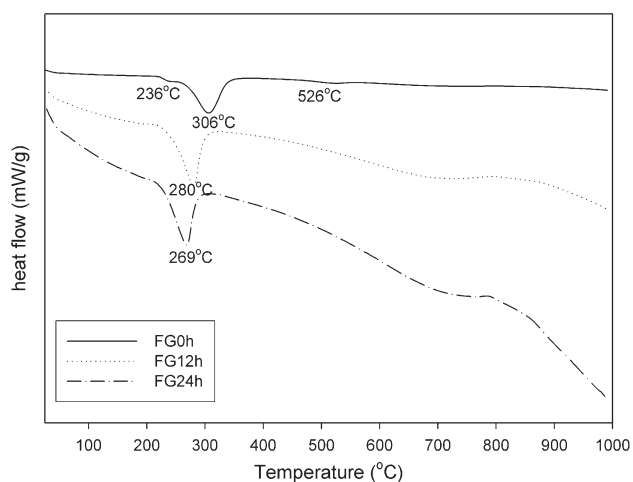


Fig. 3. The thermogravimetric curves of unmilled and milled gibbsite at various milling times.

signal, is attributed to the dehydration of gibbsite to form alumina. The endothermic peak was shifted toward the lower temperature with an increasing milling time, indicating an acceleration of the dehydration of gibbsite by the milling process.²¹ The overall weight losses of all the samples were approximately around 35%, which were in good agreement with the calculated value of 34.6% for the dehydration reaction



The dehydration of FG0h (Fig. 4(a)) in first endothermic step (236°C) was due to loss of water in the sample. The second endothermic peak (306°C) is corresponding to a weight loss of 22.5%, XRD measurements of FG0h treated at 400°C also show a peak at $2\theta = 14.4^\circ$ (Fig. 6(d)). It points out that boehmite formed at this range of temperature. In addition, the endothermic peak at around 526°C indicated that boehmite transforms to alumina. Figure 6(b) shows that diffraction peaks of mixed phases of alumina were observed at 500°C. However, this endothermic peak disappeared when milling time increased, indicating that the milling conditions affected the transformation sequence of gibbsite.¹²

XRD data were undertaken to study the transformation phases from gibbsite at various temperatures. The XRD patterns of FG0h, FG12h, and FG24h are shown in Fig. 5. The intensities of XRD peaks decreased and became wider as the milling time increased. It is due to decreasing of the crystallinity and particle size of gibbsite. Figures 6–8 shows the XRD pat-

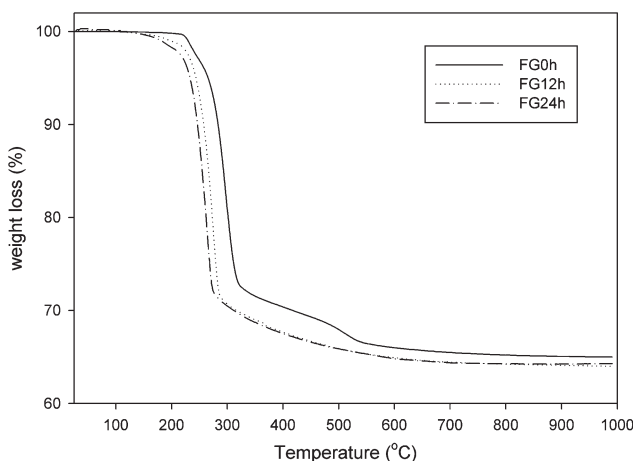


Fig. 4. The differential thermal analyses curves of unmilled and milled gibbsite at various milling times.

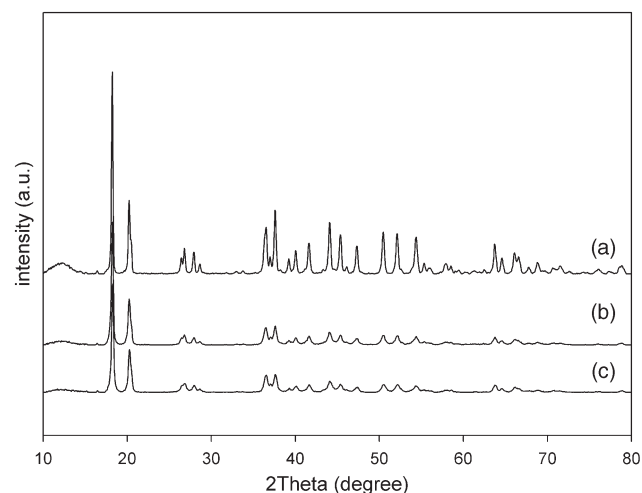


Fig. 5. The X-ray diffraction patterns of unmilled and milled gibbsite at various milling times; (a) FG0h, (b) FG12h, and (c) FG24h.

terns of calcined FG0h, FG12h, and FG24h at various temperatures. For the calcined FG12h, the mixture between boehmite and χ -phases was found at 400°C and the χ -phase was observed at a higher calcination temperature. In the case of prolonged milling (FG24h), the transformation of gibbsite to χ -alumina was completed at 350°C. This implies that the small particle sizes are effective for reduction in the transformation temperature of gibbsite to χ -alumina.²⁶

When particle size of gibbsite is small, the dominant peak ($2\theta = 14.4^\circ$) of boehmite would be reduced (Figs. 6(d) and 7(d)). As a result, χ -alumina occurred from the small particle size of gibbsite. It has been known that the dehydration sequence of gibbsite in air is affected by its particle size. In small gibbsite particles ($< 10 \mu\text{m}$), boehmite is rarely formed, but in the case of larger particles ($> 100 \mu\text{m}$), boehmite is formed because the water formed by the decomposition of the gibbsite cannot rapidly escape from the larger particles.^{2,12,20,27} Consequently, transformation of gibbsite occurred through route 1 (Fig. 1). However, the boehmite phase may be observed from the small particle size of gibbsite, if the gibbsite particle is a crystal.²⁰ Bhattacharya *et al.*²⁰ found that crystal gibbsite ($0.25 \mu\text{m}$) can produce boehmite at 400°C. Nevertheless, Jang *et al.*¹² used ground gibbsite losing the crystalline structure, and boehmite was not observed at low temperature. When FG0h was heated, boehmite was observed at 400°C and χ -alumina was formed at 450°C. However, χ -alumina was not the only phase of alumina that occurred

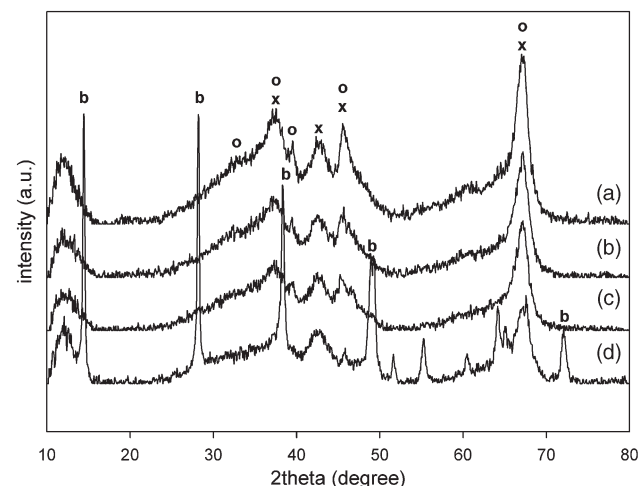


Fig. 6. The X-ray diffraction patterns of FG0h calcined at various temperatures, b, boehmite; x, χ - Al_2O_3 ; o, γ - Al_2O_3 (a) 600°C, (b) 500°C, (c) 450°C, and (d) 400°C.

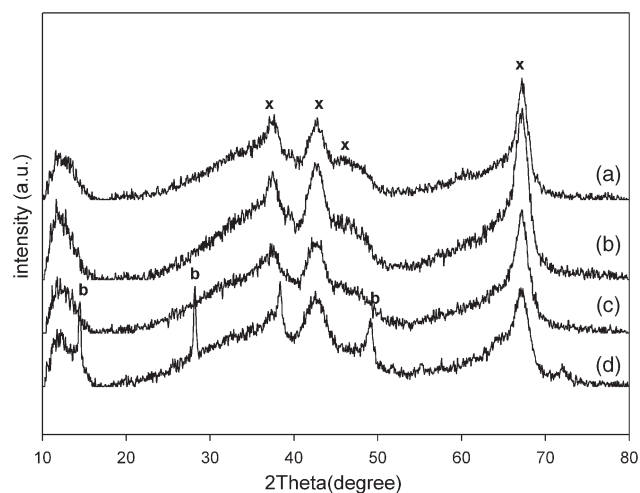


Fig. 7. The X-ray diffraction patterns of FG12h calcined at various temperatures, b, boehmite; x, γ - Al_2O_3 (a) 600°C, (b) 500°C, (c) 450°C, and (d) 400°C.

at this temperature; the peak of γ -alumina was also observed. For the micrometer sizes, both transition routes (Fig. 1) may possibly occur, which depends on the heat treatment conditions.²⁸ The decomposition of boehmite would occur at 300°C at atmospheric pressure. The typical temperature reported for the decomposition of boehmite to γ - Al_2O_3 is 450°C.²⁹

In the past, α -seeding has been shown to influence phase development and transformation kinetics of alumina.^{26,30} It may be possible that the γ peaks in Figs. 6–8 could have been enhanced by such a seeding effect. However, in the present study, the contamination from abrasives appeared to have very little impact on the reduction of transformation temperature of gibbsite to χ -alumina due to the very small amount presented. The amounts of wear debris obtained by milling the alumina balls in water for 24 h with and without gibbsite were only 2 and 3 wt% of the gibbsite weight, respectively. According to the literature, the effect of α -seeding was dependent not only on the size of the seeds but also on the amount of the seeds presented. For examples, Kano *et al.*²⁶ showed that the presence of 50 wt% α -alumina seeding reduced the transformation temperature of gibbsite to α -alumina by 120°C (from 1030° to 910°C), while for 5 wt% α -alumina seeding, the transformation temperature decreased only about 30°C. Similarly, Xie *et al.*³⁰ reported that $\text{Al}(\text{OH})_3$ can be transformed to α - Al_2O_3 at a relatively lower temperature (1100°C) with the help of seeds by wet grinding of

Table I. The BET Surface Area and Alumina Phase of Unmilled and Milled Samples after Calcination at 600°C

Samples	Phase	Surface area (m^2/g)
FG0h	—	25.1
FG0h600C	γ and χ	101.8
FG12h600C	χ	110.5
FG24h600C	χ	122.6

high-purity Al_2O_3 balls when the seed concentration was increased to > 10 wt%. Moreover, the average particle size of the abrasives in this study was much larger than those reported in the literature for reduction in the transformation temperature of gibbsite powder (i.e., 24 μm (this work) as compared with 0.6 μm in Xie *et al.*³⁰).

(3) BET Surface Area

Based on BET surface analyses of calcined samples summarized in Table I, the FG0h had significantly smaller surface area. After calcinations, the structure of gibbsite was destroyed, resulting in a drastic increase in surface area of the calcined samples. With the same calcination temperature, FG24h600C had the highest surface area of 122.6 m^2/g . The increase in the surface area of treated samples is due to the decrease in particle size. These results are in good agreement with that of Ogata *et al.*,¹⁹ who used gibbsite as the starting material and found that the specific surface area increased when the calcination temperature increased.

Table II summarizes the crystallite size (d_{XRD}) and the fraction of χ -phase of the calcined samples. It can be seen that the increase in calcination temperature resulted in a larger crystallite size. Meanwhile, the fraction of χ -alumina increased with the increasing calcination temperature. These results indicated that high-purity χ -alumina can form at the higher temperature. Du *et al.*²¹ also reported that the fraction of α -phase in α -alumina synthesized from bayerite would increase with increasing calcination temperature. Macêdo *et al.*²⁵ found that the high fraction of α -alumina can be produced from γ -alumina when the calcination temperature increased from 750° to 900°C. At low temperature (450°C), the fraction of χ -alumina rapidly increased from 0.58 to 0.89. It is implied that mechanical activation affected the formation of χ -alumina. Under isothermal condition, the fraction of χ -alumina increased when the particle size decreased. It is confirmed that the small particle size of gibbsite can produce high purity of χ -alumina. In comparison with pure χ -alumina prepared by the solvothermal method as reported previously by our group (crystallite size 6 nm and BET surface area 168 m^2/g),¹⁷ the physical properties of χ -alumina obtained by the calcination of FG24h were comparable to those of the solvothermally derived ones.

(4) Kinetics Measurements

Table III summarizes the transformation rate constants (k) of unmilled and milled gibbsite, which was calcined at different

Table II. The Particle Size (d_{XRD}) of the Samples after Calcination and the Fraction of χ -Phase

Samples	T (°C)	d_{XRD} (nm) [†]	Fraction of χ -phase [‡]
FG0h	450	3.8	0.58
	500	4.1	0.72
	600	4.4	0.88
FG12h	450	3.7	0.68
	500	3.8	0.94
	600	4.2	0.95
FG24h	450	3.3	0.90
	500	3.7	0.99
	600	3.8	1

[†]Calculated by the Scherrer equation. [‡]Calculated by quantitative XRD.

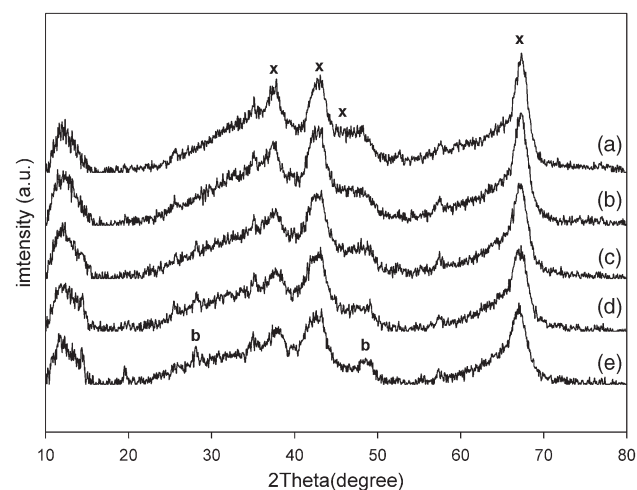


Fig. 8. The X-ray diffraction patterns of FG24h calcined at various temperatures, b, boehmite; x, γ - Al_2O_3 (a) 600°C, (b) 500°C, (c) 400°C, (d) 350°C, and (e) 300°C.

Table III. Rate Constant (k) for Milled and Unmilled Gibbsite at Different Temperature

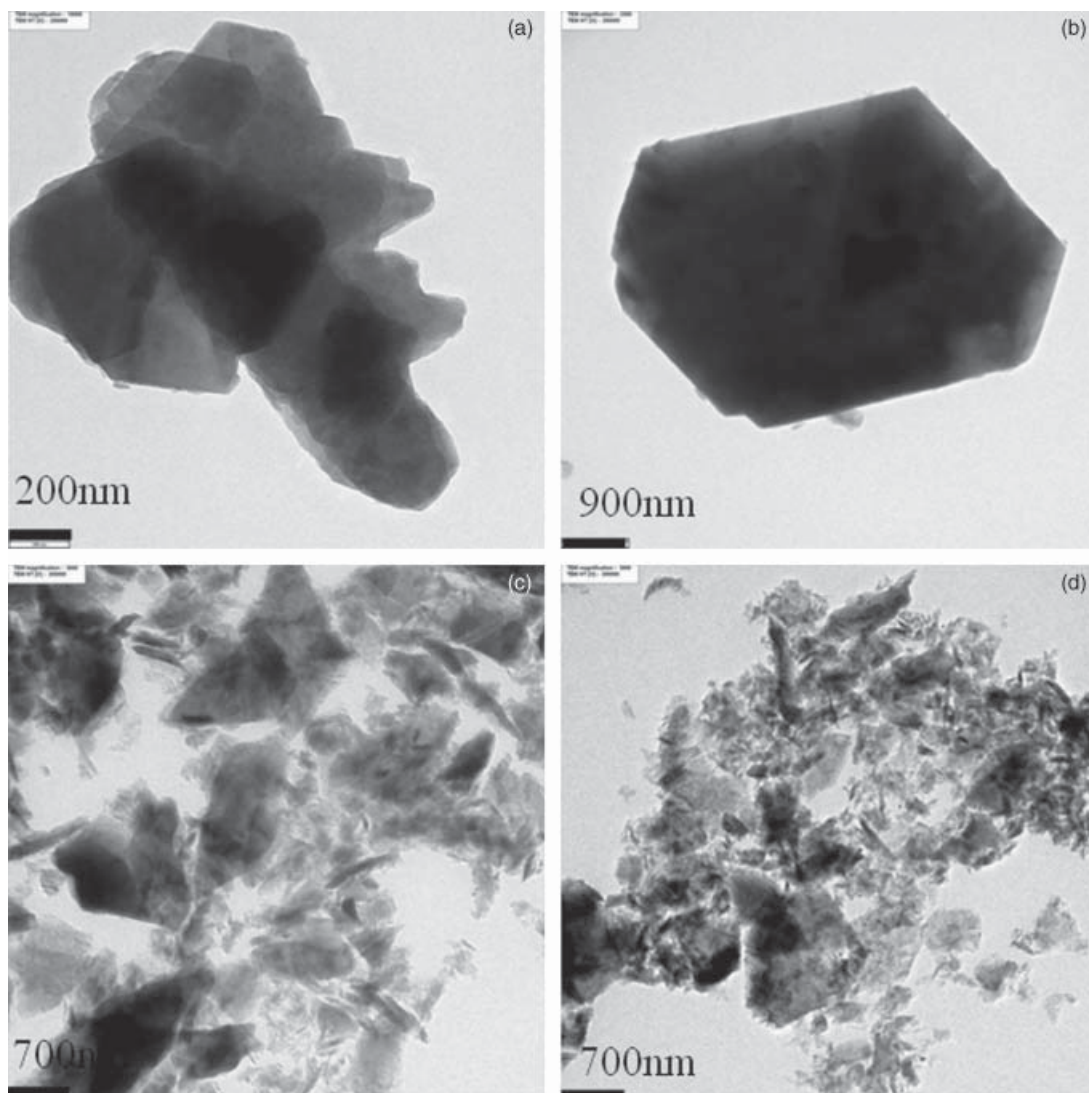
Milling time (h)	k (min^{-1})
$T = 600^\circ\text{C}$	
0	0.0142
12	0.0178
24	0.0359
$T = 500^\circ\text{C}$	
0	0.0110
12	0.0153
24	0.0248
$T = 450^\circ\text{C}$	
0	0.0033
12	0.0054
24	0.0188

temperatures. For any constant temperature, k increased with the increasing milling time. At a low temperature, the milling can increase k more significantly. For example, at 450°C activation of the sample, milling for 24 h increased the reaction rate constant 5.7 times (compared with the sample for 0 h), but at 600°C it increased only 2.5 times. Panchula and Ying³¹ synthesizing α -alumina from milled and unmilled γ -alumina reported that k increased with the increase in calcination temperature and milling time from 30 to 120 min.

Table IV. Activation Energy of Milled and Unmilled Gibbsite

Sample	E_a (kJ/mol)
FG0h	20.6
FG12h	14.7
FG24h	6.8

Table IV shows the activation energy for phase transformation of unmilled and milled gibbsite to χ -alumina. The activation energy decreased from 20.6 to 14.7 and 6.8 kJ/mol after milling for 12 and 24 h, respectively. This result indicated that the activation energy decreased with the decreasing particle size of the starting gibbsite. In general, reducing the particle size would lead to an increasing surface energy of the particle, thereby resulting in the decreasing of activation energy for phase transformation and transformation temperature as shown in the DTA profile.²⁸ The XRD patterns also confirmed that the transformation temperature of gibbsite to χ -alumina reduced from 450° to 350°C after milling for 24 h. It may be attributed to the fact that gibbsite grows to the critical size of phase transformation and then transform to χ -alumina at a lower temperature.^{28,31} Moreover, the milling of gibbsite for 12 and 24 h can be up to 28% and 67% of the activation energy compared with that of the unmilled gibbsite. Several researchers observed the kinetics of transition alumina. Macêdo *et al.*²⁵ studied the ki-

**Fig. 9.** The transmission electron micrographs of FG0h (a, b), FG12h (c), and FG24h (d).

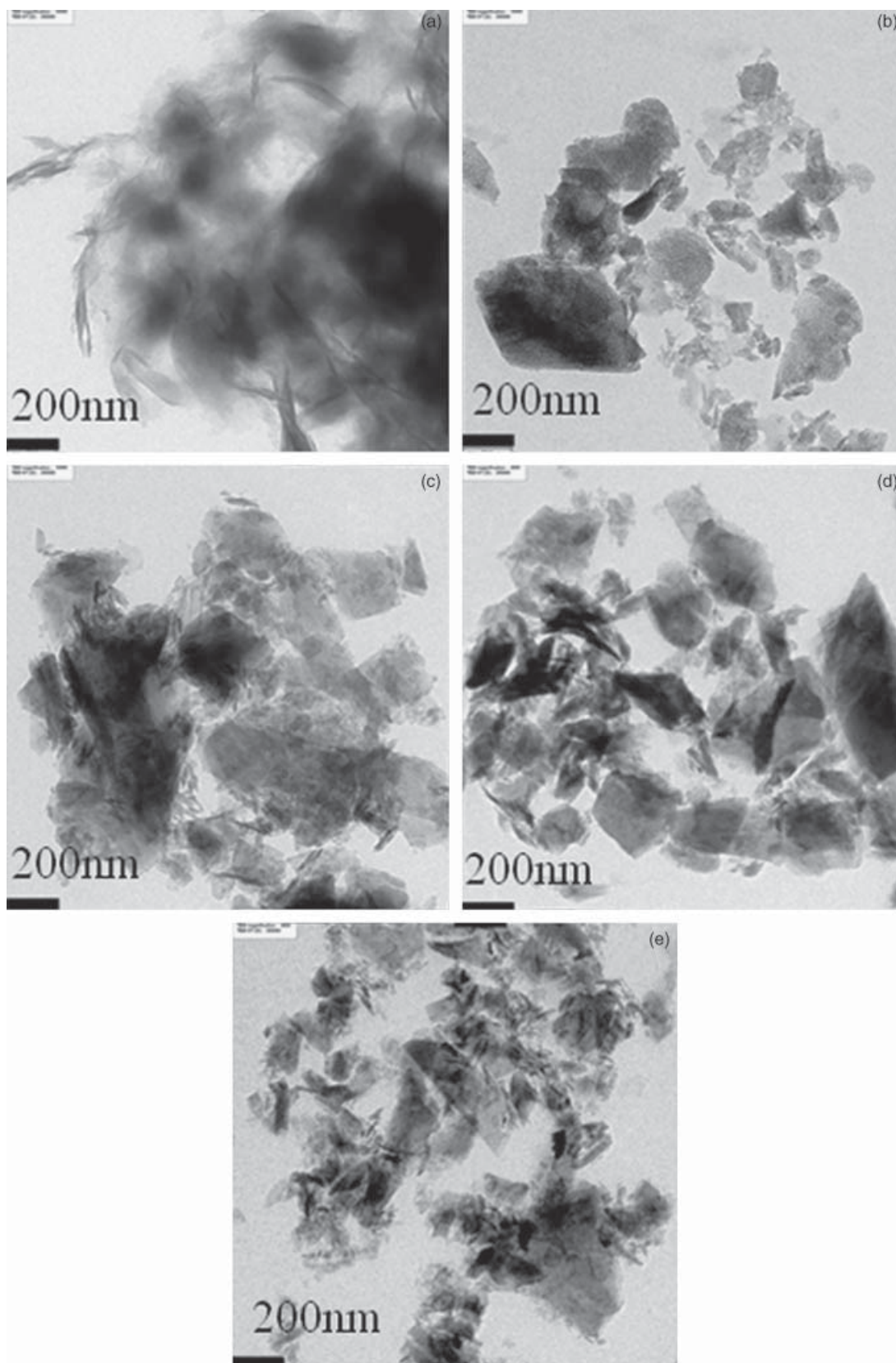


Fig. 10. The transmission electron micrographs of FG0h400C (a), FG0h600C (b), FG12h400C (c), FG12h600C (d), and FG24h600C (e).

netics of γ - to α -alumina. They found that the activation energy of this phase transformation was 201 ± 4 kJ/mol. Chang *et al.*²⁸ studied the size effect of χ -alumina to α -alumina. The activation energy reduced from 506 to 321 kJ/mol when d_{50} of χ -alumina decreased from 155 to 40, respectively. Yang *et al.*³² presented the formation during θ - Al_2O_3 to α - Al_2O_3 transformation. They

used three kinds of θ -powder (as-received, homogenized, homogenized, and additionally uniaxial-pressed compact) as the starting material. The activation energy was 299, 189, and 148 kJ/mol, respectively. Candela and Perlmutter³³ studied the kinetics of boehmite formation by the thermal decomposition of gibbsite under water vapor pressure from 100 to 3200 Pa. The

activation energy was 142 ± 10 kJ/mol. In the present work, the value of activation energy was lower than those reported in the above-mentioned works due to the lower transformation temperature.

(5) TEM Observation

The effect of grinding on the morphology of gibbsite and χ - Al_2O_3 were studied by TEM observation. Figure 9 shows the TEM micrographs of unmilled (a and b) and milled (c and d) gibbsite powder. The unmilled fine gibbsite clearly consisted of pseudohexagonal plates, while irregular and flaky particles were observed for milled samples. It revealed that the milling effectively changed the morphology of gibbsite and reduced particle size. Figures 10(a) and (b) show the TEM micrographs of FG0h400C and FG0h600C, respectively. Figure 10(a) shows that the structure is a strip. It was due to the formation of boehmite. However, this structure disappeared when gibbsite was milled for 12 h and calcined at the same temperature (Fig. 10(c)). It was probably due to the decreasing of boehmite phase in calcined samples. Figures 10(b), (d), and (e) exhibited the TEM micrographs of FG0h600C, FG12h600C, and FG24h600C, respectively. Figures 10(d) and (e) indicated that the dispersed χ -alumina with narrow size distribution was obtained from milled gibbsite, whereas the larger particle of mixed phase (χ , γ) was obtained from unmilled one (Fig. 10(b)). Besides, the morphology of samples is similar to that of gibbsite treated by mechanical milling.

IV. Conclusions

High-purity nanocrystalline χ -alumina can be produced from milled gibbsite (FG12h and FG24h). The transformation temperature of gibbsite to χ -alumina decreased from 450° to 350°C when the milling time of gibbsite was increased from 12 to 24 h, respectively. For the unmilled gibbsite (FG0h), the mixed χ and γ -phase Al_2O_3 were formed at 450°C . The fraction of χ -alumina increased with the increase in the milling time and calcination temperature. The activation energy for phase transformation of gibbsite to χ - Al_2O_3 also decreased with the reducing particle size of the starting gibbsite.

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Improvement of propane oxidation activity over Pt/Al₂O₃ by the use of MIXED γ - and χ -Al₂O₃ supports

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Abstract The use of mixed γ - and χ -phase Al₂O₃ as supports for preparation of Pt/Al₂O₃ catalysts resulted in higher acidity of Al₂O₃ and higher Pt dispersion compared to the pure phase supports. As a consequence, higher propane oxidation activities were obtained.

Keywords Chi alumina · Phase composition · Pt/Al₂O₃ · Propane oxidation

Introduction

The catalytic combustion of hydrocarbons has widely been used for power generation in gas turbine combustors and emission control of automotive exhausts. Pt/Al₂O₃ is recognized as the most active catalyst for the catalytic combustion of lower alkanes such as propane, while supported palladium catalysts are more active for methane oxidation [1–5]. The reaction mechanism of alkane oxidation over precious metal supported on alumina under oxygen rich conditions has been reported [6–9]. It is suggested that oxygen adsorbs much more effectively than alkanes resulting in high coverage of chemisorbed oxygen on the metal surface. The slowest reaction step has been postulated to be the dissociative chemisorption of alkane on the bare metal surface with breakage of the weakest C–H bond [10–13] followed by its interaction with oxygen adsorbed on an adjacent site. Many researchers reported “structure-sensitiveness” of the reaction in the case of methane

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combustion over supported metal catalysts [1, 2, 14, 15]. Yazawa et al. [16] reported that propane combustion over Pt catalysts was structure-sensitive in which the turnover frequency increased with an increase in acid strength of support materials and a decrease in platinum dispersion.

χ - Al_2O_3 is one of the metastable polymorphs of transition alumina with relatively high thermal stability compared to γ - Al_2O_3 . Nanocrystalline transition alumina has been synthesized by decomposition of aluminum isopropoxide under solvothermal conditions [17–20]. Pansanga et al. [21] showed that high catalytic activities for CO hydrogenation of Co/ Al_2O_3 can be obtained over the ones supported on mixed γ - and χ - Al_2O_3 . Mephoka et al. [22] synthesized alumina supports with various χ/γ ratios by solvothermal synthesis and found that the ones with 30–70% χ -phase Al_2O_3 gave higher Pt dispersion than pure γ -phase and improved catalytic activity in CO oxidation. In those studies, the effect of mixed γ - and χ -crystalline phase Al_2O_3 on the catalytic activity of Al_2O_3 supported catalysts in structure-insensitive reactions such as CO oxidation and CO hydrogenation has been clearly demonstrated.

Thus, it is the goal of this study to investigate the catalytic activity of the Pt catalysts supported on mixed γ - and χ - Al_2O_3 with various χ/γ ratios in a structure-sensitive reaction such as propane oxidation reaction. The catalyst activities were evaluated in terms of propane conversion and light-off temperature. The catalysts were also characterized by N_2 physisorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), C_3H_8 temperature program desorption (C_3H_8 -TPD), and NH_3 temperature program desorption (NH_3 -TPD).

Experimental

Preparation of Al_2O_3 and Pt/ Al_2O_3

Nanocrystalline Al_2O_3 samples with various χ/γ compositions were prepared by the solvothermal method using approximately 25 g of aluminum isopropoxide dissolved in a mixed solution of toluene and 1-butanol as starting materials according to the method described by Mephoka et al. [22]. The as-synthesized powders were calcined in a flow of air at 600 °C for 6 h. The 0.3% Pt/ Al_2O_3 catalysts were prepared by incipient wetness impregnation with a desired amount of an aqueous solution of hexachloroplatinic acid hexahydrate and then calcined in air at 380 °C for 2 h.

Catalyst characterization

XRD patterns of the samples were collected using a SIEMENS D-5000 X-ray diffractometer with Cu K_α radiation and a Ni filter in the 2θ range of 20°–80°. The BET surface areas were measured by N_2 adsorption–desorption isotherm at liquid nitrogen temperature (−196 °C) using a Micromeritics ASAP 2020. The morphologies of catalyst samples were determined by TEM using a JEOL JEM-2010 transmission electron microscope. C_3H_8 -TPD and NH_3 -TPD experiments were carried out using a Micromeritics Chemisorp 2750 system. The dispersion of active

Pt metals was measured using CO pulse-chemisorption technique in a flow of helium in a Micromeritics ASAP 2750.

Reaction study

Propane oxidation over various Pt/Al₂O₃ catalysts was performed in a quartz tube (i.d. 6 mm). Approximately 0.2 g of catalyst was loaded in the reactor. It was then reduced by hydrogen for 1 h at a flow rate of 100 cm³/min at 500 °C and then cooled to room temperature before the reaction. The composition of products was analyzed on-line using a gas chromatograph with a TCD detector (SHIMADZU GC 8A) with a Porapak QS column. The reaction gas of 1% C₃H₈ and 7% O₂ was fed to the catalyst bed at a space velocity of 16,000 h⁻¹. The reaction temperature was raised by 50 °C steps from 100 to 450 °C. At each temperature, the reaction products were analyzed 20 min after the bed temperature attained predetermined value.

Result and discussion

The XRD patterns of Pt/Al₂O₃ catalysts with various χ - and γ -Al₂O₃ compositions are shown in Fig. 1. All the catalyst samples exhibited the typical pattern for transition alumina without any additional peaks for Pt phases due probably to the very low amount of Pt present (0.3 wt%). Nanocrystalline Al₂O₃ supports with pure χ - and γ -phase were obtained by the reaction of aluminum isopropoxide (AIP) in toluene and 1-butanol, while the mixed-phase Al₂O₃ were obtained by the reaction in the mixed solvents. In this paper, the Pt catalysts supported on Al₂O₃ support with 0, 30, 50, 70 and 100% χ -Al₂O₃ are referred to as Pt/C0G100, Pt/C30G70, Pt/C50G50, Pt/C70G30, and Pt/C100G0, in order. The XRD characteristic peak at $2\theta = 43^\circ$ was used for the calculation of χ -phase (%) according to those reported by Meephoka et al. [22].

The TEM images of 0.3 wt% of Pt/Al₂O₃ containing different compositions of γ - and of χ -phase Al₂O₃ are shown in Fig. 2. The wrinkled sheet morphology was attributed to the presence of γ -Al₂O₃ while χ -Al₂O₃ were shown as spherical particles [17], [23], [24]. As the percent χ -Al₂O₃ increased, the wrinkled sheets morphology became less apparent and more spherical particles structure was seen. However, Pt/PtO metal clusters/particles were not distinguishable in all the TEM images.

The acidity of the Pt/Al₂O₃ catalysts was determined by NH₃-TPD experiments and the results are shown in Fig. 3. Two broad peaks with a maximum temperature at 80–110 °C and 290–310 °C were observed in all cases. Compared to the pure phase Al₂O₃, the mixed-phases showed a slight peak shift toward higher temperature. The amounts of NH₃ adsorbed on Pt/Al₂O₃ catalysts were calculated from the peak areas and the results are given in Table 1. The results indicated that acidity of Pt/Al₂O₃ was higher and stronger when they were supported on the mixed γ - and of χ -phase Al₂O₃ than those supported on the pure phase ones.

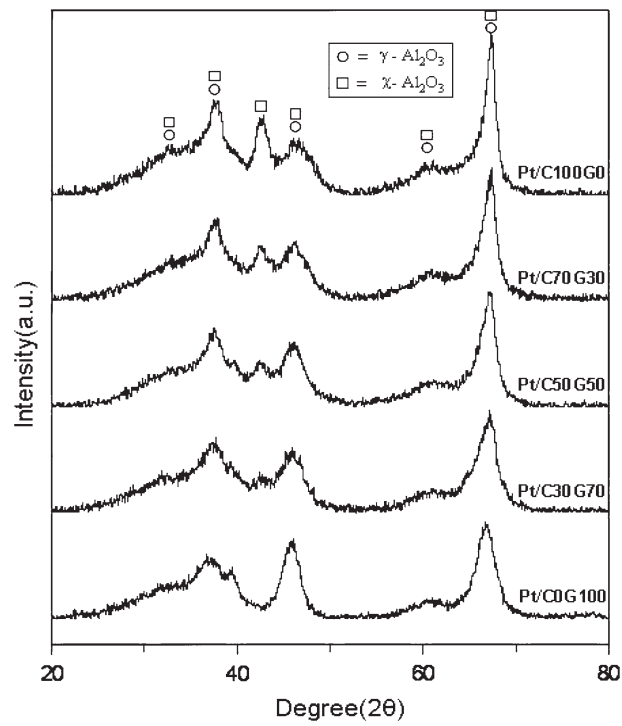


Fig. 1 XRD patterns of 0.3% Pt/ Al_2O_3 catalyst

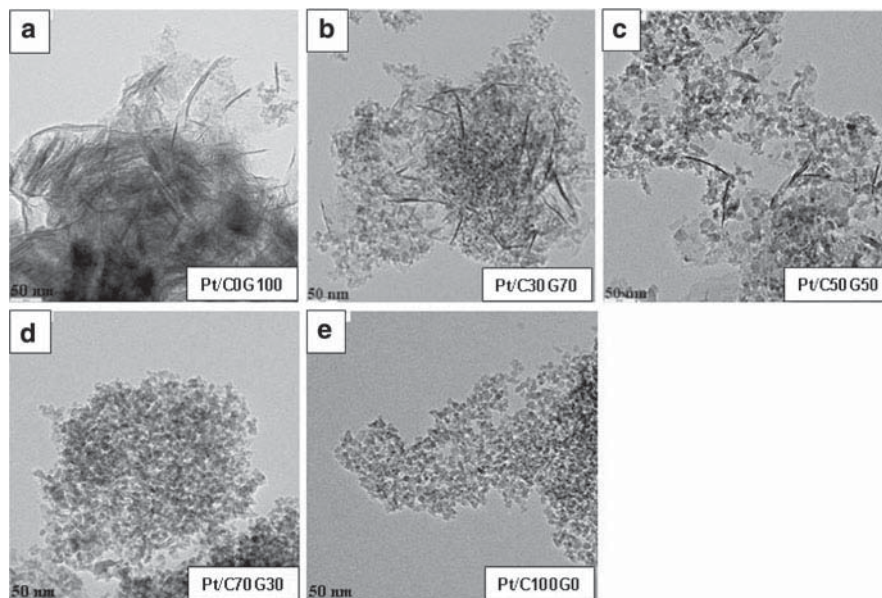


Fig. 2 TEM images of 0.3% Pt/ Al_2O_3 catalyst with various phase composition

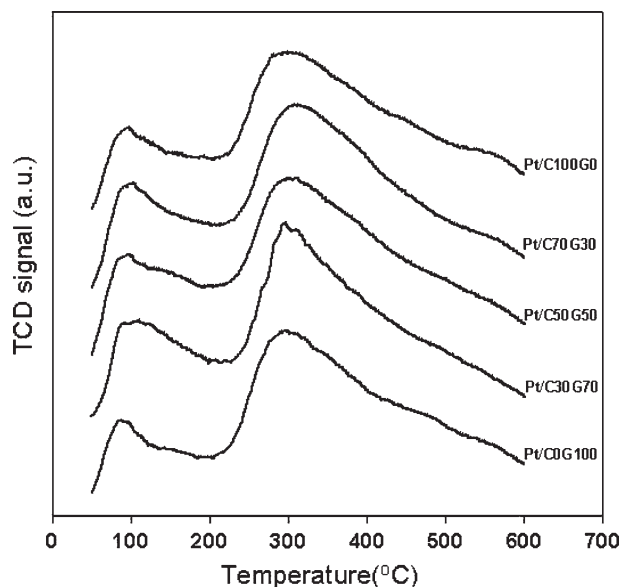


Fig. 3 NH_3 -TPD profiles of catalysts with various phase composition

Table 1 Physiochemical properties of 0.3% Pt/ Al_2O_3 catalyst

Sample	BET surface area (m^2/g) ^a	Crystallite size (nm)	Acidity ($\mu\text{mol g}^{-1}$) ^b	CO chemisorption $\times 10^{-18}$ (molecule CO/g catalyst) ^c	Pt dispersion (%) ^d
Pt/C0G100	203	5	733	3.25	38.9
Pt/C30G70	189	5	768	3.56	42.6
Pt/C50G50	177	6	775	3.55	42.5
Pt/C70G30	163	6	770	3.58	42.8
Pt/C100G0	151	6	724	3.18	38.1

^a Error = 4%, SD = 5.1

^b Error = 3%, SD = 13.4

^c Error = 3%, SD = 0.1

^d Error = 3%, SD = 0.9

The BET surface area, crystallite size, and CO chemisorptions results of the Pt/ Al_2O_3 catalysts are summarized in Table 1. The BET surface area decreased from 203 to 151 m^2/g as the χ -phase content increased from 0 to 100% although the average crystallite size of Al_2O_3 supports remained constant at around 5 to 6 nm. The amounts of active Pt metals on the catalyst surface were calculated from CO chemisorption experiments at room temperature. The calculation of Pt active sites was based on the assumption that one carbon monoxide molecule adsorbs on one platinum site. The metal active sites of Pt supported on pure χ - and γ - Al_2O_3 were

essentially similar at around 3.2×10^{18} molecules CO/g cat., while the active sites of Pt supported on mixed phase Al_2O_3 (30, 50, and 70% of χ -phase) were higher than those on the pure phase Al_2O_3 (approximately 3.6×10^{18} molecules CO/g cat.). This can be explained by the difference between particle morphologies of the different alumina phase structures.

The characteristics of the surface active sites of Pt/ Al_2O_3 catalysts were studied by means of the temperature programmed desorption of C_3H_8 from 50–500 °C and the results are shown in Fig. 4. The major C_3H_8 desorption peak appeared at ca. 425 °C for those supported on the single phase Al_2O_3 (either pure γ - or χ - Al_2O_3). It is clearly seen that the same peak was significantly shifted towards lower temperature (to ca. 320 °C) for the Pt/ Al_2O_3 catalysts containing mixed γ - and χ - Al_2O_3 supports. It is suggested that the Pt may interact more strongly on the mixed Al_2O_3 structures than on the single phase ones so that the adsorption strength of C_3H_8 was altered (lower).

Fig. 5 shows the activities of Pt/ Al_2O_3 catalysts in propane oxidation as a function of reaction temperature. The catalytic activity of supported platinum catalyst depended on the platinum dispersion. Moreover, the activity of Pt-based catalysts for propane combustion also increased with increasing support acidity. A similar trend has been reported by Garetto et al. [25]. Since the C_3H_8 -TPD experiments showed that propane desorption behaviors were different between the mixed phase Al_2O_3 supported Pt catalysts and the single phase supported ones. Faster desorption of C_3H_8 from Pt surface would, therefore, result in more active Pt surface available for reaction to proceed; as a consequence an increase in oxidation activity was obtained. According to the reaction mechanism in the literature, the rate of propane oxidation increases by increasing the active sites for both dissociation

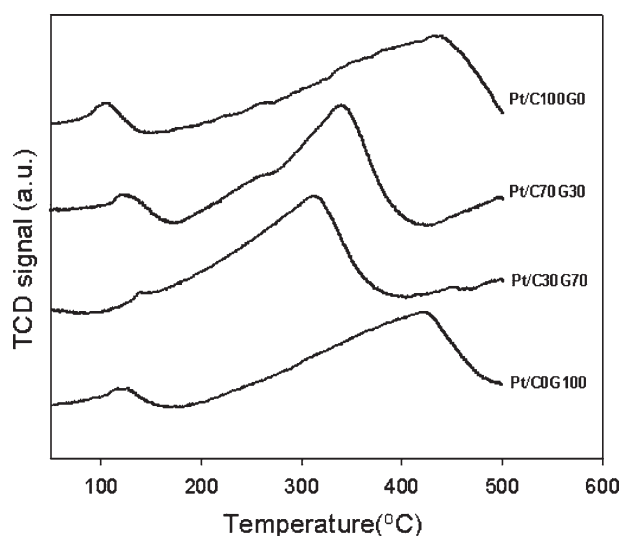


Fig. 4 C_3H_8 -TPD profiles of catalysts with various phase composition

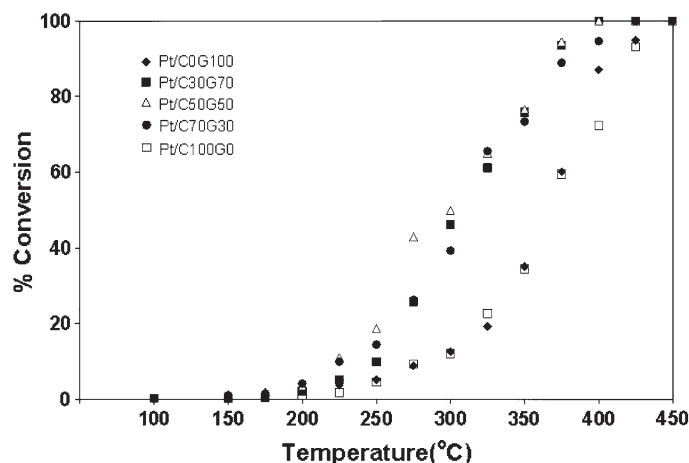


Fig. 5 C_3H_8 conversion profiles of 0.3% Pt/ Al_2O_3 for the propane oxidation

of C–H bond and oxygen adsorption [8, 10, 26]. The advantages of mixed phase composition effect on the activity and selectivity characteristics have also been reported for other catalyst systems [22, 23, 27–29].

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Solvent effect on synthesis of zirconia support for tungstated zirconia catalysts

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ABSTRACT

Solvothermal reaction of zirconium *n*-butoxide (ZNB) in different solvent media, such as 1,3-pentanediol, 1,4-butanediol, 1,5-pentanediol and 1,6-hexanediol resulted in the formation of zirconium dioxide (ZrO₂) nanostructure. Then, the 15%W/ZrO₂ (WZ) catalysts using different zirconia supports were prepared by impregnation method. The effects of solvent on preparation of zirconia on the catalytic performance of WZ catalysts in esterification of acetic acid and methanol at 60 °C were investigated. The experimental results showed that ZrO₂ particles prepared in 1,4-butanediol (ZrO₂-BG) have a spherical shape, while in other glycols the samples were irregularly-shaped particles. The reaction results of esterification illustrated that the W/ZrO₂-BG catalysts had high surface acidity and showed high acetic acid conversion. The W/ZrO₂-PeG catalysts (ZrO₂ particles prepared in 1,5-pentanediol, PeG) exhibited the lowest surface acidity among other samples due to strong interaction of proton species and the zirconia supports as proven by TGA. One of the possible reasons can be attributed to different amounts of carbon residue on the surface of catalysts.

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1. Introduction

Tungstated zirconia [WO_x/ZrO₂ (WZ)] catalysts have attracted much attention because of their ability to catalyze a wide range of reactions, such as dehydration [1], isomerization [2–4], and esterification [5,6]. The advantages of WO_x/ZrO₂, such as higher stability under high-temperature treatments and reductive atmospheres, lower deactivation rates during catalysis, and easier regeneration [7–9] are of considerable interest for practical applications in the petrochemical industry. Several authors revealed that the catalytic properties of WO_x/ZrO₂ only depend on the W surface density (W/nm²). This surface density can be modified by varying the tungsten loading and the calcination temperature [10–12]. The tungsten oxide overlayer can be present as isolated surface monotungstates, polymeric surface polytungstates, and crystalline WO₃ particles on the oxide supports [13].

Since the preparation of tungstated zirconia by impregnation of hydrated zirconia was reported by Hino and Arata [14], several investigations about the influence of the preparation method on the activity of WO_x/ZrO₂ materials have been investigated [15–17]. Some of the general conclusions are that the incorporation of tungsten into the zirconia favors the formation of the

tetragonal phase, inhibits sintering of the support and enhances the acid strength of these solids by the slight reduction of the WO_x species. Since then, many papers have been focused on the properties of catalysts prepared from zirconium oxyhydroxide [7,15,18–25]. Systems based on the W deposited on crystallized zirconia were studied to a smaller extent [3,4,6,26–28]. In addition, the influences of the initial state of the support on the acidic properties of the catalyst and their relation with the activity and surface structure are not fully understood. Recently, we have reported the characteristics and catalytic behaviors of tungstated zirconia catalysts, which can be altered by different calcination atmospheres [6]. It revealed that the presence of F-center (electrons stabilized in oxygen vacancies) on zirconia surface occurred during reduction treatments leading to enhancement of activity for tungstated zirconia catalyst due to the formation of monotungstate surface morphology resulted into high acidity of the catalyst.

In the present study, four different solvent media were used to prepare the nanocrystalline zirconia prepared by the solvothermal method. The application of synthesized zirconia as supports for tungsten catalysts was further investigated. The influences of the solvent used during preparation on the physicochemical properties of the zirconia were investigated by means of N₂ physisorption, XRD, XPS, and SEM. The corresponding solvothermal-derived zirconia supported tungsten catalysts were further characterized by Raman spectroscopy, TGA, XPS and were tested for catalytic activities in the acetic acid esterification reaction.

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2. Experimental

2.1. Preparation of zirconia

Zirconium dioxide was prepared by methods previously reported [6]. Approximately 25 g of zirconium tetra-*n*-butoxide 80 wt% solution in 1-butanol (ZNB, Aldrich) was suspended in 100 ml of the desired solvent in a test tube, which was then placed in a 300 ml autoclave. The solvents used in this work were 1,3-propanediol (PG, purity 98%, Aldrich), 1,4-butanediol (BG, purity 99%, Sigma–Aldrich), 1,5-pentanediol (PeG, purity 98%, Merck) and 1,6-hexanediol (HG, purity 97%, Merck). The gap between autoclave wall and the test tube was filled with 30 ml of the same solvent. The autoclave was completely sealed and purged with nitrogen, the mixture was heated to 300 °C at a heating rate of 2.5 °C/min and was kept at that temperature for 2 h. After cooling to room temperature, the resulting powders were collected after repeated washing with methanol by centrifugation. The products were then air-dried and were used without further calcinations.

2.2. Preparation of W/ZrO₂

The zirconia samples obtained from 2.1 were used as supports. The zirconia doped with tungsten catalysts were prepared by the incipient wetness impregnation method using tungsten (VI) chloride (WCl₆, Aldrich, 99.9%) sufficient for yield materials having 15 wt% of W loading. The catalysts were dried at 110 °C for 12 h and calcined in air at 500 °C for 3 h.

2.3. Catalyst nomenclature

The different solvothermal-derived zirconia supports are designated as ZrO₂-PG, ZrO₂-BG, ZrO₂-PeG and ZrO₂-HG in which PG, BG, PeG and HG refer to the solvent used (PG = 1,3-propanediol, BG = 1,4-butanediol, PeG = 1,5-pentanediol and HG = 1,6-hexanediol). The tungsten catalysts supported on different zirconia supports are designated as W/ZrO₂-PG, W/ZrO₂-BG, W/ZrO₂-PeG and W/ZrO₂-HG.

2.4. Catalyst characterization

2.4.1. XRD measurements

X-ray powder diffractograms of various investigated samples were determined using a D5000 (Siemens) using Ni filter Cu K α radiation from 20° to 80°. Crystallite size was calculated from the Scherrer equation using 1 0 1 diffraction peak of tetragonal zirconia. The fraction of tetragonal (f_t) phase in the W/ZrO₂ catalysts are estimated by the following formula [22]

$$f_t = \frac{A_t(101)}{A_{\text{tot}}(\text{ZrO}_2)} \quad (1)$$

where $A_t(101)$ stands for the area of the (1 0 1) peak of the tetragonal phase and A_{tot} the area of all the tetragonal and monoclinic peaks in the pattern.

2.4.2. Surface area measurements

The specific surface areas (S_{BET}) of various samples were determined from nitrogen adsorption studies conducted at –196 °C in a Micrometrics ASAP 2020 device. Prior to the adsorption measurements, the sample was degassed at 300 °C for 3 h under reduced pressure of 10^{–3} mmHg.

2.4.3. Acidity measurements

The number of acid sites was also estimated by using a method involving an aqueous ion-exchange step of the catalyst H⁺ ions with Na⁺ ions, followed by titration of the resulting solution [29].

2.4.4. Raman spectroscopy

The molecular structure of the supported tungsten oxide phases was determined using Raman spectroscopy since this technique has the ability to discriminate between the different tungsten oxide molecular structures [2,14,16,19]. The Raman spectra of the samples were recorded using a PerkinElmer Spectrum GX spectrometer, collected by projecting a continuous wave YAG laser of Nd (810 nm) through the samples at room temperature. A scanning range of 700–1400 cm^{–1} with a resolution of 2 cm^{–1} was applied.

2.4.5. X-ray photoelectron spectroscopy (XPS)

The XPS measurement was carried out using an AMICUS photoelectron spectrometer equipped with an Mg K α X-ray as a primary excitation and KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at a pass energy of 75 kV. All the binding energies were referenced to the C 1s peak at 285.0 eV of the surface adventitious carbon.

2.4.6. Thermogravimetric analysis (TGA)

TGA was performed using a TA Instruments SDT Q 600 analyzer. The samples of 10–20 mg and a temperature ramping from room temperature up to 800 °C at 10 °C/min were used in the operation. The carrier gas was N₂ UHP.

2.4.7. Electron spin resonance spectroscopy (ESR)

JEOL JESRE2X A model ESR was used to measure the surface F-center and Zr³⁺ on the surface of ZrO₂ and W/ZrO₂ [30]. Before measurement, the sample was dried at 120 °C overnight. A 0.1 g of sample was placed in a sample tube, which was sealed at atmospheric pressure and room temperature.

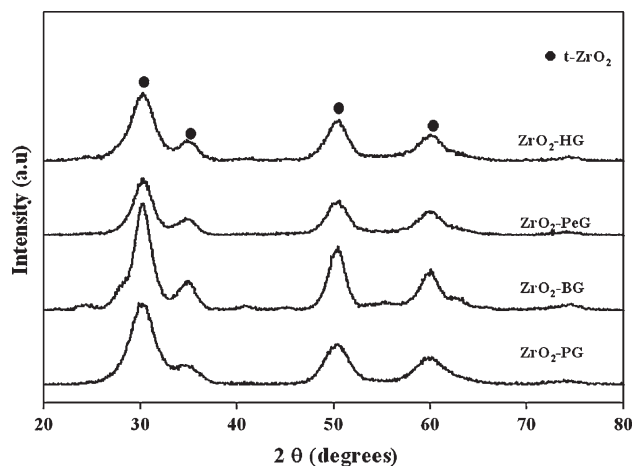
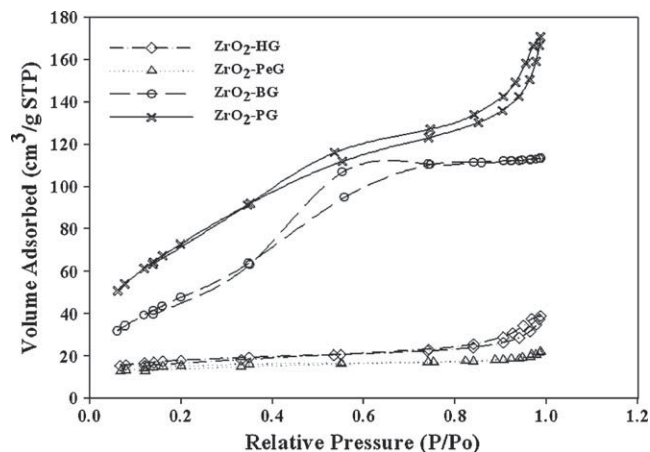
2.5. Activity test

The activity test was performed on the basis of esterification reaction between acetic acid and methanol. The reaction was conducted at 60 °C with magnetic stirring in a closed 250 ml regular glass reactor using 20 g of acetic acid (99.9%) and 2 wt% of catalyst heated to the desired temperature, and the methanol (99.9%) was then added to the mixture (3 eq. molar). Sample was withdrawn periodically from the reactor, quenched to room temperature, and centrifuged in order to separate the solid catalyst from product to prevent further reaction. Concentration of reacted samples was determined using a SHIMADZU gas chromatograph (GC–14B) equipped with Chrompack SE52 column and flame ionization detector. UHP N₂ was used as the carrier gas. Reactions were tested in batch process for 6 h.

3. Results and discussion

3.1. Textural properties and crystalline structure of the catalysts

The X-ray diffraction patterns of the zirconia powders prepared by the solvothermal method in various solvents are shown in Fig. 1. The XRD patterns indicate only tetragonal crystalline zirconia (*t*-ZrO₂) for all as-synthesized products. No other crystal structures were observed. The average crystallite sizes calculated from the XRD line broadening using the Scherrer equation and the BET surface areas of the zirconia are reported in Table 1. The average crystallite sizes of zirconia were approximately 2.7–4.0 nm. Within experimental error, there was significant difference in the crystallite sizes and BET surface areas of the zirconia prepared in different glycols, the crystallization pathway of zirconia in the various glycols is probably different [31]. The isotherms of products obtained from ZNB with different glycols are shown in Fig. 2. The isotherms of all parent materials are of IV type (IUPAC

Fig. 1. XRD patterns of the ZrO_2 .Fig. 2. Typical adsorption/desorption isotherms of the ZrO_2 .

classification) with a capillary condensation step above $0.4 P/P_0$, which is typical of ordered mesoporous structures. Fig. 3a–d shows SEM images of the products synthesized in 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol and 1,6-hexanediol, respectively. It was reported that when the starting material were completely dissolved into the glycol, nanocrystals were formed [32]. Each particle was, therefore, a single crystal grown from a nucleus. It was found that the samples prepared in 1,4-butanediol have a

spherical shape and a dense mass while in other glycols the samples were irregularly-shaped particles. The secondary particles which appeared as separate spherical particles when prepared in 1,4-butanediol seem to be formed by aggregation of primary particles. These results were found to be in agreement with our previous work [33]. It has been proposed by Kongwudthiti et al. [31] that the mechanisms during crystallization of zirconia in the different glycols were completely different. The ESR was used to

Table 1

Textural characterization of zirconia supports.

Sample	Crystallite size (nm)	XRD phases	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore Size (nm)
ZrO_2 -PG	2.7	<i>t</i> - ZrO_2	276	0.29	3.60
ZrO_2 -BG	4.0	<i>t</i> - ZrO_2	184	0.19	2.69
ZrO_2 -PeG	3.1	<i>t</i> - ZrO_2	54	0.02	3.84
ZrO_2 -HG	2.8	<i>t</i> - ZrO_2	63	0.05	5.70

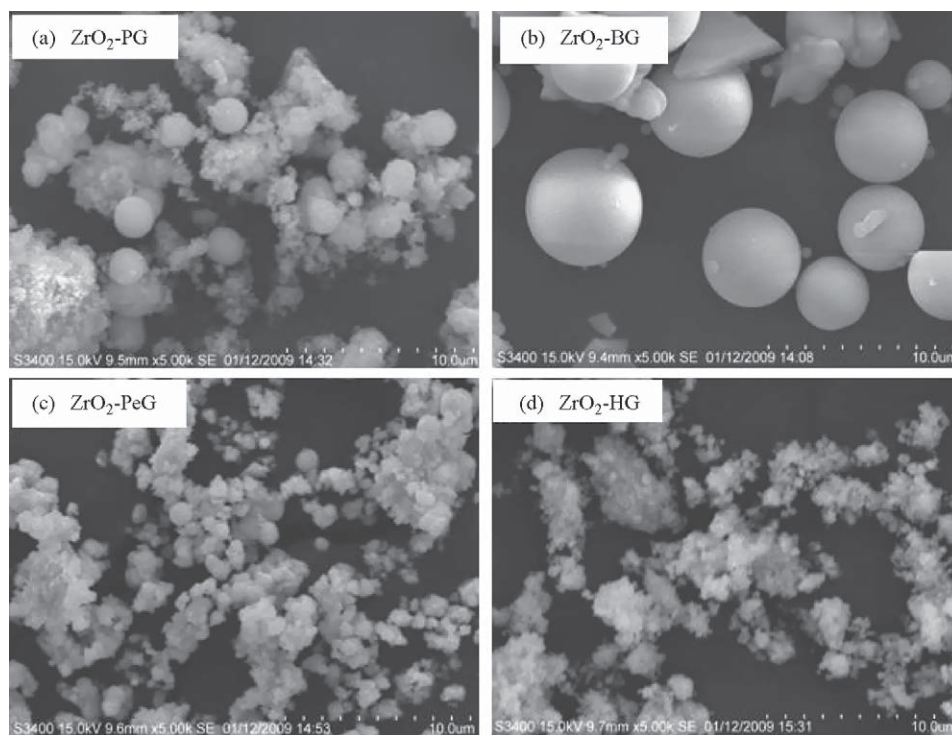
Fig. 3. SEM micrographs of (a) ZrO_2 -PG (b) ZrO_2 -BG (c) ZrO_2 -PeG, and (d) ZrO_2 -HG.

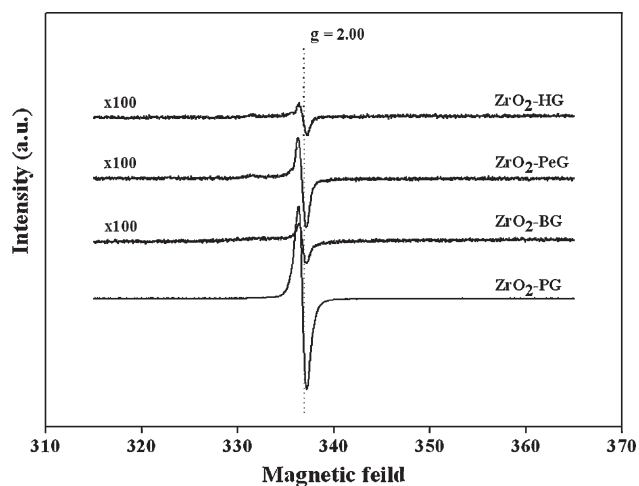
Table 2Physicochemical properties of W/ZrO₂ catalysts.

Sample	Crystallite size (nm)	XRD phases	Fraction of tetragonal phase ^a	BET surface area (m ² /g)	W surface density (W-atom/nm ²)	Surface acidity ^b (μmol/g)	Monotungstate/polytungstate intensity ratio
W/ZrO ₂ -PG	4.6	<i>t</i> -ZrO ₂ , <i>m</i> -ZrO ₂	0.41	79	6.2	70	1.8
W/ZrO ₂ -BG	4.6	<i>t</i> -ZrO ₂ , <i>m</i> -ZrO ₂	0.50	124	3.9	110	2.8
W/ZrO ₂ -PeG	3.6	<i>t</i> -ZrO ₂ , <i>m</i> -ZrO ₂	0.36	49	10.0	55	1.1
W/ZrO ₂ -HG	3.1	<i>t</i> -ZrO ₂ , <i>m</i> -ZrO ₂	0.43	62	7.9	75	2.5

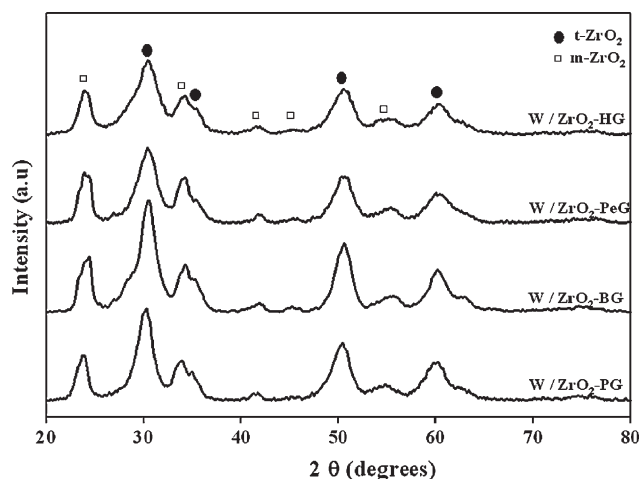
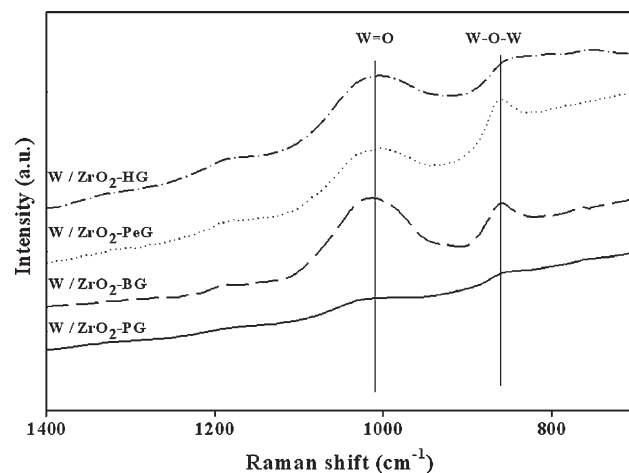
^a Calculated from tetragonal zirconia (101) reflection from the equation $f_t = \frac{A_t(101)}{A_{tot}(ZrO_2)}$.^b Measured by ion-exchange and titration with 0.05 N NaOH.

identify the surface nature of ZrO₂. The ESR spectra of all samples show a symmetrical singlet with $g = 2.00$ assigned to F-center, i.e., electrons stabilized in oxygen vacancies [34,35] as shown in Fig. 4. According to the present results, the order of F-center of zirconia prepared by different solvents was as follows: ZrO₂-PG > ZrO₂-PeG > ZrO₂-BG > ZrO₂-HG, which should be the origin of the formation of different morphologies for ZrO₂ in the specified system.

The characteristics of various tungstated zirconia catalysts are shown in Table 2. In this study, the zirconia was impregnated with 15 wt% of tungsten and calcined in air at 500 °C for 3 h. The BET surface areas of the tungstated zirconia catalysts were slightly less than that of the original zirconia supports suggesting that tungsten was deposited in some of the pores of zirconia. This loss of surface area is significantly inhibited by the presence of WO_x species [36] or the emergence of monoclinic zirconia (*m*-ZrO₂). Among all these catalysts, W/ZrO₂-BG shows higher surface area followed by W/ZrO₂-PG, W/ZrO₂-HG, and W/ZrO₂-PeG, respectively. Based on the values of surface area (at different solvents) and the same amount of W loading, it is possible to estimate nominal W surface densities [37]. The W surface coverage of W/ZrO₂-BG sample can be achieved at the density of 3.9 W-atom/nm², which was in good agreement with monotungstates surface coverage value (0–4 W/nm²) reported by earlier works [10]. While the W surface coverage of W/ZrO₂-PG, W/ZrO₂-PeG and W/ZrO₂-HG are more than 4 W-atom/nm² (6.2, 10.0 and 7.9 W-atom/nm², respectively). The X-ray diffraction patterns of the tungstated zirconia catalysts are shown in Fig. 5. The XRD patterns of W/ZrO₂ revealed the partial phase transformation from *t*-ZrO₂ to *m*-ZrO₂ in all samples due to calcination temperature with W loading. No diffraction peaks of WO₃ crystallites ($2\theta = 23.2^\circ$, 23.6° and 24.48°) were observed for all samples, indicating that tungsten oxide was well dispersed on zirconia. It should be noted that the XRD peak at ca. 24.3° for all samples was assigned to the monoclinic zirconia and not WO_x crystallites [38].

**Fig. 4.** ESR spectra of the ZrO₂.

The Raman spectra of W/ZrO₂ catalysts are shown in Fig. 6. The Raman spectra of the tungsten oxide component are generally found at the 700–1400 cm⁻¹ region because the strong crystalline ZrO₂ support vibrations tend to dominate the spectra below 700 cm⁻¹ [39,40]. Crystalline WO₃ shows characteristic Raman bands at 807, 715, and 274 cm⁻¹ [41]. Absence of these bands indicates that microcrystalline WO₃ is not formed on the surface of W/ZrO₂ catalyst. These results are in well agreement with the XRD results, where no independent peaks due to crystalline WO₃ are observed. All the catalysts show broad bands of two components at 1020 and 850 cm⁻¹, which are attributed to the symmetric stretch of the terminal W=O of monotungstate and asymmetric stretch of the W–O–W bonds of polytungstate, respectively [27,41], indicating that polytungstates coexist with monotungstate under monolayer

**Fig. 5.** XRD patterns for W/ZrO₂ calcined at 500 °C for 3 h.**Fig. 6.** Raman spectra of various W/ZrO₂.

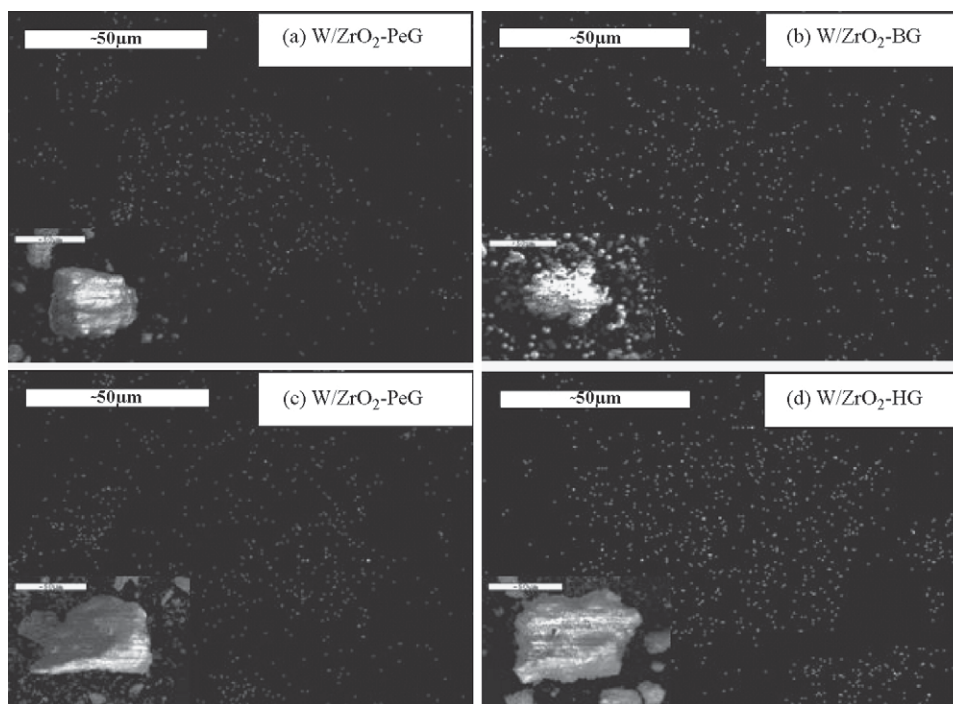
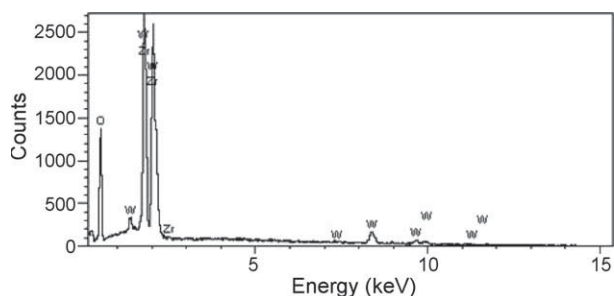


Fig. 7. SEM/EDX mapping for W distributions of (a) W/ZrO₂-PG, (b) W/ZrO₂-BG, (c) W/ZrO₂-PG, and (d) W/ZrO₂-PG.

coverage. Moreover, the complex WO_x feature could be resolved by curve fitting procedures only in the range 800–1200 cm⁻¹ (not shown here), the surface monotungstate/polytungstate ratio of W/ZrO₂-BG (ca. 2.8) is larger than those prepared with other solvents as shown in Table 2. The elemental distribution was also performed using SEM/EDX mapping on the external surface. The W distribution in the various supports is shown in Fig. 7. As seen, all samples exhibited good distributions of W without any changes in the zirconia morphology. The typical measurement curve for the quantitative analysis using EDX is shown in Fig. 8. The amounts of W in various zirconia are also listed. Results revealed that the ZrO₂-BG exhibited the lowest amount of W present on the surface, which can be attributed to the monotungstates surface coverage. The ESR signals for all tungstated zirconia catalysts are shown in Fig. 9. All catalysts exhibited the ESR signals of Zr³⁺ ($g_{\perp} = 1.97$, i.e., oxygen vacancy site) and F-center. It is known that the intensity of F-

center signal on zirconia surface is disproportional to that of Zr³⁺ signal [34,35]. The amounts of Zr³⁺ present on the surface of zirconia are in the following order as; W/ZrO₂-PeG > W/ZrO₂-HG > W/ZrO₂-BG > W/ZrO₂-PG. It is known from previous work [6] that by calcinations in reductive and oxidative ambient, the electronic density can move to F-center and Zr³⁺. In addition we found that the presence of F-center on zirconia surface is able to enhance the catalytic activity of tungstated zirconia catalyst. However, in our present work, the highest amounts of F-center on the surface of ZrO₂-PG did not show the highest activity of tungstated zirconia catalysts. It is therefore possible to explain these results by carbon residue on the surface of catalysts obtained from the XPS analysis (Table 3). The carbon residues on the surface of catalyst were found to be in the order: W/ZrO₂-PeG > W/ZrO₂-PG > W/ZrO₂-HG > W/ZrO₂-BG. On the other words, the higher amounts of carbon residue on zirconia, the lower activity of WZ catalyst was.



Catalysts	W (Atomic %)
W/ZrO ₂ -PG	2.26
W/ZrO ₂ -BG	1.33
W/ZrO ₂ -PeG	1.35
W/ZrO ₂ -HG	1.74

Fig. 8. A typical EDX spectrum for a W/ZrO₂ catalyst.

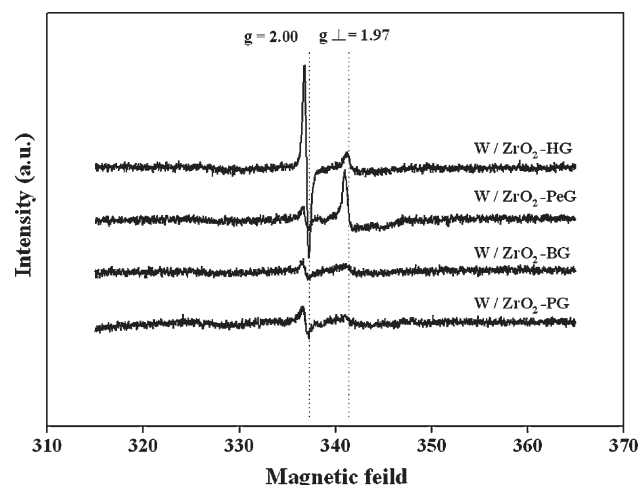


Fig. 9. ESR spectra of various W/ZrO₂ catalysts.

Table 3
XPS results.

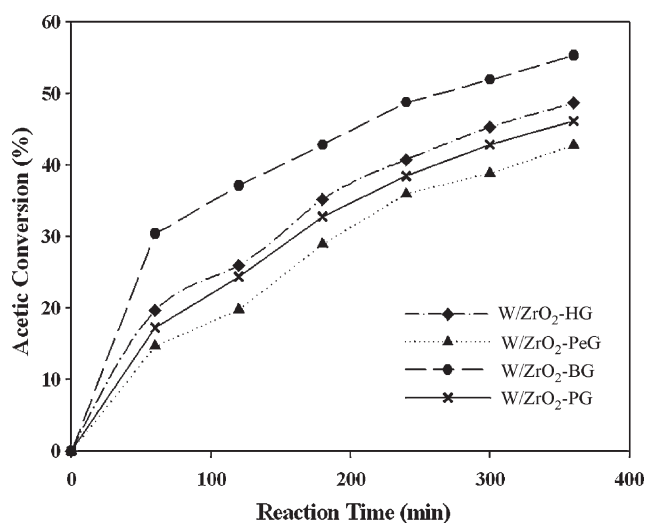
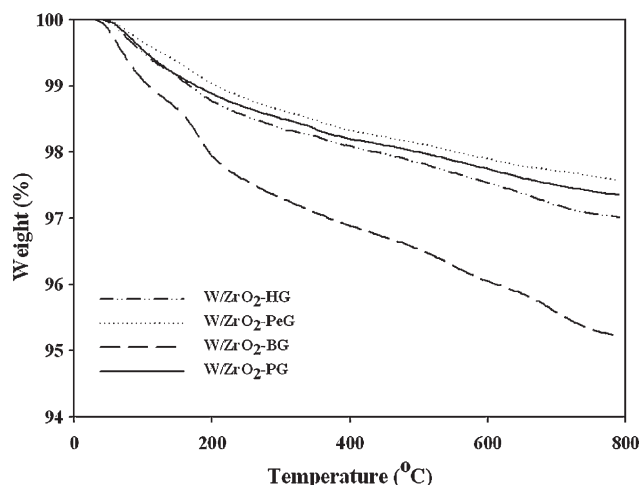
Sample	B.E. (eV)			Atomic concentration			
	Zr 3d	O 1s	W 4f	W/Zr	W/O	Zr/O	C (%)
ZrO ₂ -PG	184.4	531.0	–	–	–	0.267	42.74
ZrO ₂ -BG	184.1	530.2	–	–	–	0.330	11.91
ZrO ₂ -PeG	185.1	531.3	–	–	–	0.337	39.86
ZrO ₂ -HG	184.3	530.5	–	–	–	0.334	30.89
W/ZrO ₂ -PG	185.7	531.3	36.2	0.311	0.079	0.265	29.74
W/ZrO ₂ -BG	184.9	530.7	36.6	0.146	0.047	0.320	14.04
W/ZrO ₂ -PeG	185.0	531.3	35.0	0.377	0.098	0.260	36.74
W/ZrO ₂ -HG	185.5	530.8	37.7	0.171	0.054	0.314	23.49

3.2. Surface acidity of the samples

In order to form a catalytically active form, it is usually necessary to anchor the amorphous WO_x with ZrO₂ tetragonal crystal phase [5,14,41]. Surface acidity is the most important function of tungstated zirconia. The acidity measurements of the catalysts by means of acid-base titration with NaOH allow us to estimate the surface acidity. It was found that they are in the range of ca. 70, 110, 55 and 75 $\mu\text{mol/g}$ for W/ZrO₂-PG, W/ZrO₂-BG, W/ZrO₂-PeG and W/ZrO₂-HG samples, respectively (Table 2). It was observed that for W/ZrO₂-BG catalyst showed the highest surface acidity among all catalysts. The number of acid sites decreases in parallel with the increase of W surface density content. Probably as a result of the generation of new acid sites due to interaction and dispersion of WO_x on the surface of the support. When the dispersion of WO_x is maximum (at the theoretical monolayer coverage) for W/ZrO₂-BG sample, the acidity is maximum. Moreover, samples with higher W surface density content show loss of acidity that is probably due to the agglomeration of WO_x on the surface.

3.3. Reaction study

Acetic acid conversion in the esterification reaction of acetic acid and methanol over the four tungstated zirconia catalysts as mentioned before were shown in Fig. 10, indicating increased conversion in the order of: W/ZrO₂-PeG < W/ZrO₂-PG < W/ZrO₂-HG < W/ZrO₂-BG. The increased activity of W/ZrO₂-BG can be attributed to its higher acidity as observed from acid-base titration techniques (Table 2). It is well known that the W surface density

**Fig. 10.** Catalytic activity on the different W/ZrO₂ catalysts.**Fig. 11.** TGA profiles of various W/ZrO₂ catalysts.

content of the catalysts and the formation of WO_x surface species is an essential factor for remaining the acidity of the catalysts, which may greatly influence the catalytic activity [10–28]. The formation of WO_x surface species was observed by Raman spectroscopy. Based on this study, activity of catalyst is related to the increasing surface monotungstate/polytungstate ratio with surface tungsten oxide coverage. One of the possible reasons is that the interaction and dispersion of WO_x on the surface of the support. The degree of interaction between the zirconia and adsorbed species can be determined by the TGA measurement [42–45]. The TGA profiles for all catalysts are shown in Fig. 11, indicating similar profiles for various supports showing the desorption of similar species. We observed that the weight losses of samples were in the order of W/ZrO₂-BG (4.8%) > W/ZrO₂-HG (3.0%) > W/ZrO₂-PG (2.7%) > W/ZrO₂-PeG (2.4%). This indicated that adsorbed species present on ZrO₂-PeG had the strongest interaction, and thus the lowest observed esterification activity. The adsorbed species are presumably involving with desorption of oxygenated and proton species relating to acidity of catalysts [46]. As seen, the carbon residue on the surface of catalysts apparently resulted in increased interaction leading to decreased acidity of catalysts. It should be mentioned that the acetic acid conversion in this present study was less than our previous work [6]. This was due to different calcination treatments for ZrO₂ prepared from the same solvent. As mentioned in the previous work [6], the H₂ treatment during calcination can result in increased F-center of ZrO₂ samples leading to increased catalytic activity.

4. Conclusions

This study revealed the effects of solvent on morphology and other characteristics of zirconia and their performance as tungstated zirconia catalyst. It was found that a series of WO_x/ZrO₂ catalysts exhibited the tungsten density in the range of 3.9 to 10.0 W-atoms/nm². XRD and Raman spectroscopy results indicated that the W phase is present as a surface interaction species. No evidence for the formation of WO₃ was found. The zirconia prepared in 1,4-butanediol as the support resulted in the highest surface acidity consequently having the highest activity. The lower activities of tungstated zirconia catalysts prepared in other solvents were due to stronger interaction of proton species and the zirconia supports as shown by weight losses of samples in the TGA profiles. The types of solvent used for preparation of the glycothermal-derived zirconia may affect the amount of carbon residue and WO_x monotungstate/polytungstate ratio on the

surface of catalysts resulting in the difference in proton species-support interaction behavior.

Acknowledgments

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The Role of Zirconia Surface on Catalytic Activity of Tungstated Zirconia via Two-Phase Esterification of Acetic Acid and 1-Heptanol

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Abstract It is proven that surface nature of zirconia can play crucial roles on determining the catalytic activity of tungstated zirconia catalysts. The solvothermal method for preparation of crystalline zirconia support can result in the formation of Zr–OH bond on its surface. This surface species related to the Zr-heteropolyacid, acting as strong Brønsted acid sites. It consequently affected on the catalytic activity.

Keywords Zirconia · Tungstated zirconia · Solvothermal method · Zr–OH bond · Zr-heteropolyacid

1 Introduction

Currently, the replacement of homogeneous catalysts with suitable heterogeneous ones is a major key to develop many processes, since heterogeneous catalysts are environmental friendly and potentially used for a long time and/or multiple reaction cycles. Moreover, it readily allows for the implementation of continuous processes. Interestingly, the heterogeneous catalyst demonstrated the remarkable performance for two-phase esterification system (organic and aqueous phases). It has been also known that the replacement of adsorbed water molecule by acetic acid molecule was only carried out by a solid acid catalyst. In our previous study [1], we reported that the Amberlyst 15 exhibited higher turnover number (TON) than sulfuric acid

(H₂SO₄) in the two-phase acid catalyzed esterification of dilute acetic acid and 1-heptanol. It was proposed that the Amberlyst 15 with adsorbed acetic acid on active sites can move into the organic phase (upper phase) by agitator, and then react with 1-heptanol leading to increased catalytic activity because the reaction occurs in the organic phase. In addition, increased activity can be also attributed to the decrease of solvation effect by water.

A heterogeneous catalyst as a tungsten oxide supported on zirconia (WZ) has been tremendously used for alkane isomerization [2–5], alcohol dehydration [6, 7] and recently biodiesel forming reaction [8–13]. This is because of their acid properties, stability under reducing and oxidizing conditions and regenerability [14]. The nature of active site is a key factor in order to achieve the high catalytic performance. For instance, the calcination temperature and tungsten loading affects on the structure of WO_x presented in an isolated surface monotungstates, polymeric surface polytungstates and crystalline WO₃ particles on a zirconia support as reported in numerous studies [3, 4, 6, 7, 15, 16]. Barton et al. [4] reported that the maximum activity for tungsten loading was slightly rather than monolayer coverage, so called polytungstate species for hydrocarbon isomerization. Gregorio et al. [17] suggested that the 15% of tungsten loading is a critical value to achieve high activity, selectivity, and stability of the catalyst on stream and good activity for saturated hydrocarbon isomerization. Lopez et al. [11] reported that the calcination temperature of 800 °C contributed with tungsten oxide polymeric structure can achieve the highest catalytic activity for both esterification and transesterification. In many cases, the preparation method of zirconia is allowing to make different surface species formed [18–21]. The generation of new active sites on the surface can bring about various influences on activity and selectivity

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for certain types of reactions [22]. Lebarbier et al. [23] reported that no significant effect of the initial form of the support (Zr oxyhydroxide versus predominantly tetragonal zirconia) was observed for *n*-hexane isomerization. Wongmaneevil et al. [24] found that the calcination of ZrO₂ support in the reductive atmosphere (H₂) can achieve higher conversion for esterification of acetic acid than that of oxidative atmosphere (O₂). Although, the numerous studies have been investigated, the influence of the ZrO₂ support on the acid properties of the WZ catalysts and their relation with the activity and surface structure are still unclear.

This work has been focused on the behaviors of surface nature for the ZrO₂ support prepared by the solvothermal method before and after loading of 15 wt% of tungsten. Based on the similar texture properties, non-treated ZrO₂ support (crystalline zirconia bonding with hydroxide, Zr–OH) was compared to the thermal treated ZrO₂ under H₂ as a reduction atmosphere (crystalline zirconia, ZrO₂). All catalyst characteristics have been investigated by means of XRD, N₂ physisorption, FT-IR spectroscopy, Raman spectroscopy, and electron spin resonance (ESR). The two-phase esterification of dilute acetic acid and 1-heptanol was performed to measure the catalytic activity of WZ catalysts in a batch reactor. This is due to the outstanding properties of WZ (distribution of acid site between Brønsted and Lewis acid sites) that would gain more beneficial for the two-phase esterification, which requires the heterogeneous catalyzed reaction [6, 12, 25, 26].

2 Experimental

2.1 Materials

Acetic acid (99.8%) and 1-heptanol (99%) were purchased from Merck and used as received. Heptyl acetate (98%) as standard of product was purchased from Wako Pure Chemical Industries. Tungstated zirconia (WZ-X) was prepared as described in Sect. 2.2

Aldrich) in a test tube, which was then placed in a 300 mL autoclave. A 30 mL of 1,4-butanediol was filled in the gap between the test tube and the autoclave wall. The autoclave was purged with nitrogen. The mixture was heated to 300 °C at a rate of 2.5 °C/min. The temperature was held constantly at 300 °C for 2 h. After reaction, this autoclave was cooled and the resulting powder yield was repeatedly washed with methanol by centrifugation. Subsequently, they were dried in air and designated as Z-NT (non-treated zirconia). Another ZrO₂ support was treated at 400 °C with heating rate of 10 °C/min under flowing H₂ atmosphere (UHP grade of gases from TIG) for 2 h, designated as Z-H₂ (H₂ treated zirconia).

Tungstated zirconia (WZ) catalysts were prepared by the incipient wetness impregnation of zirconia with an aqueous solution of WCl₆ to obtain the final catalyst having 15 wt% of tungsten loading. The hydrolysis of WCl₆ possibly resulted in the well dispersion of WCl₆ species in the aqueous solution, which is corresponding to work reported by Kob et al. [28]. This probably leads to obtain well dispersion on the zirconia support. The freshly impregnated catalyst was dried at 110 °C for 12 h. Then, it was calcined at 500 °C for 3 h [24]. The retained chlorine on WZ catalyst was less than 10 ppm, which was verified by the AgNO₃ titration with K₂CrO₄ indicator. The nomenclatures given as WZ-NT and WZ-H₂ were used for the tungstated on non-treated zirconia and H₂ treated zirconia surface, respectively.

2.3 Catalysts Characterization

Powder X-ray diffraction (XRD) was performed by SIEMENS XRD D5000 using CuK_α radiation. The average crystallite size was determined using Scherrer's equation calculated from peak broadening as applied to the tetragonal (101) peak.

Physical properties, such as BET surface area (*S*_{BET}), pore diameters and BJH cumulative pore volumes were evaluated with N₂ adsorption–desorption at –196 °C in a Micromeritics ASAP 2020 [12]. The tungsten surface density was calculated based on the BET surface area of WZ and tungsten loading (15 wt%) as follows [24, 29]:

$$\text{Surface density} = \frac{\text{Promoter loading (\%)} / 100 \times 6.023 \times 10^{23}}{\text{Formula weight of promoter} \times \text{BET surface area (m}^2/\text{g}^{-1}) \times 100^{18}}$$

2.2 Catalyst Preparation

Zirconia as a support was prepared via a solvothermal method as reported by Kongwudthiti et al. [27]. Zirconium tetra-*n*-butoxide 80 wt% solution in 1-butanol (Aldrich) was suspended in 100 mL of 1,4-butanediol (99%, Sigma-

A JEOL, JESRE2X model electron spin resonance spectroscopy (ESR) was used to measure the surface F-center and Zr³⁺ on the surface of ZrO₂ and WZ. Before measurement, the sample was dried at 110 °C overnight. 0.1 g of sample was placed in a sample tube, which was sealed at atmospheric pressure and room temperature.

FT-IR analysis of ZrO_2 support was carried out in a Nicolet model 6700 of the IR spectrometer using the wave-number ranging from 400 to $4,000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . A small amount of sample (0.2 g) was thoroughly mixed with ground KBr in an agate mortar and pressed as pellets.

The Raman spectra of the samples were collected by projecting a continuous wave YAG laser of Nd (810 nm) through samples at room temperature. A scanning range of $200\text{--}1,400\text{ cm}^{-1}$ with a resolution of 2 cm^{-1} was applied.

2.4 Reaction Test

The catalyst activity via the esterification reaction between dilute acetic acid (6 wt%) and 1-heptanol was conducted in a stirred batch reflux system at temperature 90°C . A three-necked flask equipped with a condenser and stirrer was charged with certain amount of 6 wt% of dilute acetic acid (6.8 mL) and catalyst samples (0.3 g). Then, the system was heated up to the reaction temperature after which the pre-heated heptanol (3.2 mL) was added. Sufficient stirring of the mixture was used to avoid external mass or heat transport limitations. The reaction temperature was maintained by means of a thermostatic paraffin bath in which the reactor was immersed. For catalytic activity measurement, samples were diluted with 2-propanol (10 mL) to stop reaction and perform in a single phase, and then analyzed by GC (Shimadzu) equipped with a flame ionization detector and Chrompack SE52 column. The reaction was repeated at different reaction times in order to obtain the acetic conversion profiles. All catalysts were employed under similar reaction conditions. GC analysis confirmed that no by-products were formed. The acetic acid conversion (%) was calculated as follows:

$$\begin{aligned} & \% \text{ acetic acid conversion} \\ &= \frac{\text{initial acetic acid conc.} - \text{acetic acid conc. at time } (t)}{\text{initial acetic acid conc.}} \\ & \times 100 \end{aligned}$$

3 Results and Discussion

Upon different treatments of zirconia, it was observed that the color of Z-NT was white, whereas the color of the Z- H_2 changed from white to dark yellow with the treatment of H_2 . This suggested that the thermal treatment under reductive atmosphere generated the F-center (color center) [30] due to the strong Zr–O bond energy that is less likely reduced by H_2 [24]. However, the color of catalyst (WZ and WZ- H_2) has returned to white again after calcination because re-oxidation was obtained [2]. This phenomenon supports the hypothesis in the color change with the presence of F-center which is only observed on the Z- H_2

support. Figure 1 shows the XRD patterns of ZrO_2 support as synthesized (Z-NT) and treated in H_2 atmosphere (Z- H_2). Tetragonal phase (t- ZrO_2) is the primary crystalline structure for Z-NT and Z- H_2 with the diffraction peaks at 30.2 , 35.3 and 49.8° [11]. A crystallite size was calculated from Scherrer's equation of the tetragonal (101) peak [31] as shown in Table 1. After the thermal treatment under reduction atmosphere (H_2) was applied on the ZrO_2 , it was found that the crystallite size and the fraction of tetragonal phase structure of Z- H_2 were still similar to those of Z-NT sample. The crystallite sizes of WZ-NT (4.5 nm) and WZ- H_2 (4.7 nm) were slightly larger than those zirconia supports before the tungsten loading when increasing of the calcination temperature to 500°C . The increase calcination temperature was also allowing to present a fraction of monoclinic phase (m- ZrO_2) with the diffraction peak at 24.3° (Fig. 1), which is in agreement with the work reported by Wongmaneevil [24]. For this study, the deposit of tungsten did not exhibit to stabilize t- ZrO_2 phase because the impregnation method appeared to permit tungsten being present on the ZrO_2 crystallite surface. It is known that the co-precipitation and sol–gel synthesis are the methods for incorporating tungsten atom into ZrO_2 lattice, which stabilizes the tetragonal structure [18, 19, 32]. WO_3 , on the other hand, has not been detected for both WZ-NT and WZ- H_2 . This may be due to either relatively low calcination temperature or tungsten loading [3, 4, 6, 7, 16, 33].

The catalyst textural properties determined by the BET method and acid site concentrations as measured by ion-exchange titration are listed in Table 1. The surface areas of Z- H_2 and Z-NT were comparable within the experimental error. This result suggested that the reductive calcination treatment did not affect on the surface area as corresponding to our previous study [24]. In general, the

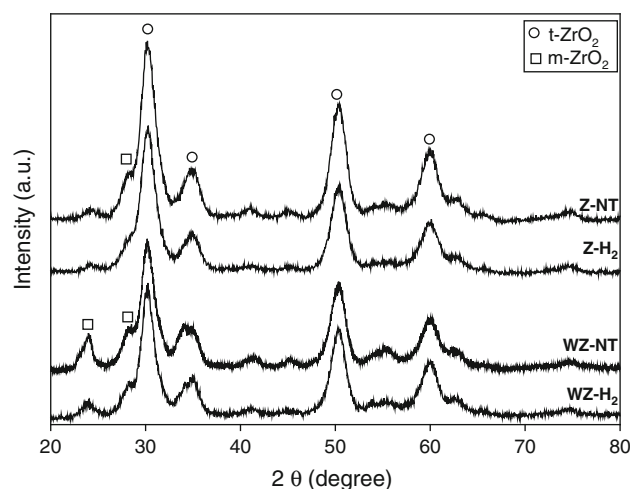


Fig. 1 XRD patterns for ZrO_2 supports and WZ catalysts

Table 1 Surface area, theoretical W surface density, surface acidity, crystallite size and XRD phases for ZrO₂ support and WZ samples

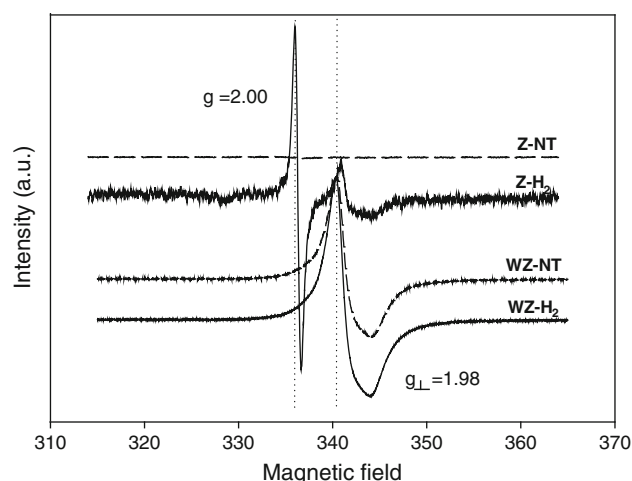
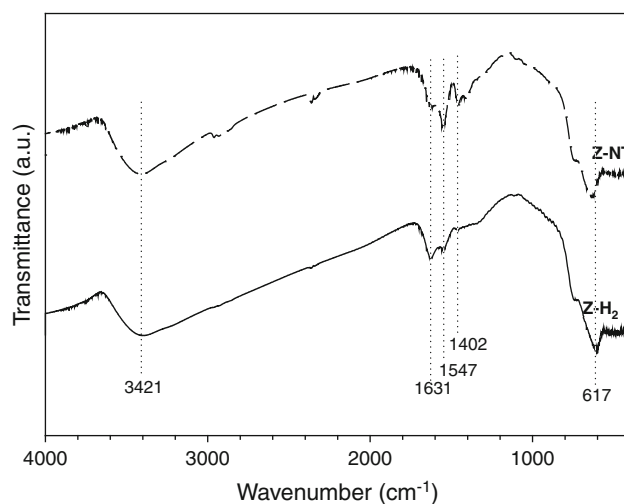
Sample	BET surface area (m ² /g) ^a	W surface density (W-atom/nm ²)	Surface acidity by exchange/titration (μmol/g) ^b	Crystallite size (nm)	XRD phases
Z-NT	161	–	–	4.1	t-ZrO ₂ , m-ZrO ₂
Z-H ₂	155	–	–	4.3	t-ZrO ₂
WZ-NT	125	3.93	233.0	4.5	t-ZrO ₂ , m-ZrO ₂
WZ-H ₂	125	3.93	133.0	4.7	t-ZrO ₂ , m-ZrO ₂

^a Experimental error ± 7%^b Experimental error ± 10%

penetration of tungsten species into the pore of ZrO₂ support could reduce the surface area of WZ-NT and WZ-H₂ [34]. In order to estimate the theoretical nominal W surface densities, WZ surface area and amount of tungsten loading were used [29]. It was found that the W surface coverage of both WZ-NT and WZ-H₂ were presented as the growing surface polytungstated domain and crystalline of WO₃ (~4 W atom/nm²) [15, 35, 36].

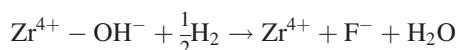
The other physical properties, such as crystallite size, tetragonal structure, and BET surface area for both Z-H₂ and Z-NT were almost similar, except for the surface defect. The electron spin resonance (ESR) spectroscopy is one of the most powerful techniques used to detect the structural defect, as shown in Fig. 2. The ESR signal of ZrO₂ can be found with g values, $g_{\perp} = 1.97$ assigned to Zr³⁺ [37] and $g = 2.00$ assigned to F-center [38]. As seen, no ESR signal for the Z-NT sample was observed in the magnetic field ranging between 310 and 370 indicating that no defect occurred on the surface of Z-NT sample. When the ZrO₂ was treated in a reductive atmosphere (H₂), the F-center was present. The dominated intensity of F-center on Z-H₂ may be produced by the reduction of hydroxyl group on ZrO₂ surface, which is corresponding to the previous reports [24, 30, 39, 40]. Due to the strong Zr–O bond energy, H₂ may not reduce the ZrO₂ surface allowing to insignificant intensity of Zr³⁺ obtained [37]. The ESR spectra of WZ catalysts were also illustrated in Fig. 2. WZ catalysts were in the oxidation atmosphere during the deposition of tungsten onto ZrO₂ support. Thus, the ESR signals of Zr³⁺ were detected on the ZrO₂ support for both WZ-NT and WZ-H₂ because the oxygen coordinatively unsaturated Zr sites under oxidation atmosphere [40]. In addition, the shift of F-center (V_{O}^{-}) to Zr³⁺ ($g_{\perp} = 1.97$) for WZ-H₂ was also observed within a good agreement to the previous reports [24, 30].

FT-IR spectroscopy was used to clarify the chemical bonding of ZrO₂ support obtained by different thermal treatments in the range of 400–4,000 cm^{−1} as presented in Fig. 3. It was found that five transmittance peaks were observed over this range. A very broad band with the highest frequency at 3,421 cm^{−1} contributed to the

**Fig. 2** ESR spectra of ZrO₂ supports and WZ catalysts**Fig. 3** FT-IR spectra of ZrO₂ supports

physically adsorbed water molecular as reported in those literatures [41–43]. In addition, the band at 1,631 cm^{−1} should be attributed to the OH group of free water related to alcohol. The IR band within the range of 617–632 cm^{−1} was corresponding to the bond of metal and oxygen (Zr–O)

as presented for both ZrO_2 supports [43]. There were other two peaks observed at 1,547 and 1,402 cm^{-1} , which are corresponding to the metal and hydroxide (Zr-OH) bond [42, 43]. It can be concluded that ZrO_2 supported prepared from solvothermal method [27] exhibited the Zr-OH group. However, this metal hydroxide bond can be eliminated by the thermal treatment in the reduction atmosphere (H_2) indicated by the decrement of these characteristic peaks. The FT-IR spectrum of ZrO_2 support is corresponding to the ESR signal with the presence of F-center on the Zr-H_2 surface. Therefore, the F-center is probably produced by the reduction of hydroxyl group on ZrO_2 surface through the following reaction [39, 40]:



In order to obtain a better insight for the changes upon molecular level structure of the tungsten oxide overlayer for WZ catalysts, the Raman spectroscopy was performed as seen in Fig. 4. The Raman bands at 310, 402, and 473 cm^{-1} were assigned to the tetragonal phase of ZrO_2 [11, 35, 44] as presented in both catalysts. Both WZ-NT and WZ- H_2 showed the characteristic peak of the terminal W=O band of the dehydrated surface WO_x species at 910–1,030 cm^{-1} [11, 36]. The WZ- H_2 exhibited slightly higher intensity of crystalline WO_3 nano-particle (799 cm^{-1}) than that of WZ-NT. The crystalline WO_3 nano-particle was observed upon the W surface density at $\sim 4 \text{ W/nm}^2$ as reported by Wachs et al. [36]. The stretching and bending modes of the bridging for W-O-W were assigned at ~ 500 –800 and ~ 200 –300 cm^{-1} [35, 45]. As illustrated in Fig. 4, WZ-NT had higher intensity of bending mode of the bridging W-O-W than that for the WZ- H_2 , whereas the stretching modes of bridging W-O-W were comparable. In summary, three different tungsten species (W=O , WO_3 , and W-O-W) were observed for both catalysts, which

were probably due to the similar W surface density at $\sim 4 \text{ W/nm}^2$.

As known, acidity of WZ catalyst is a key factor to enhance the catalytic activity for several reactions by generation of active sites [2–13]. The catalytic active sites were plausible for high surface acidity form with a monolayer of polytungstated species (WO_x) [3, 4, 11]. The surface acidity was obtained from a larger population of Brønsted acid sites and the presence of stronger Brønsted acid sites [19]. WZ-NT and WZ- H_2 catalysts exhibited the growing surface polytungstated domain and crystalline of WO_3 nano-particle. It is more likely to obtain the similar Brønsted acid site density based on the similar polytungstated domain. However, the WZ-NT has higher acidity compared to WZ- H_2 as presented in Table 1. The higher surface acidity of WZ-NT should be derived from the different forms of polytungstated domain. The FT-IR spectra of zirconia support suggested that the Zr-OH bonding presented in Z-NT appeared to result in a super acid center (heteropolyacid of W, $[\text{XW}_{12}\text{O}_{40}]^{3-}$), which was proposed by Afanasiev et al. [46] and Scheithauer et al. [18, 44, 47]. In addition, the Raman spectrum of WZ-NT was resemble the finger print of Raman spectrum of tungstophosphoric heteropolyacid ($\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$) as a super acid [45]. The only substantial difference between the WZ-NT and WZ- H_2 catalysts in the monolayer region is the presence of the Zr-heteropolyacid spices for the WZ-NT catalysts as illustrated in Scheme 1. The catalytic activity sites seem to be fully oxidized from noncrystalline surface polytungstate networks incorporating trace levels of surface-exposed Zr capable of stabilizing delocalized protons for Brønsted acid sites as well as heteropolyacids did [18, 44, 47].

As expected, after 9 h reaction period, WZ-NT exhibited 17% higher for an acetic acid conversion than that for WZ- H_2 , as shown in Fig. 4. Heteropolyacid as the strong Brønsted acid sites related to acid site density and catalytic activity of esterification as corresponding to the work reported by Park et al. [48]. This could be obtained from the crystalline zirconia with Zr-OH bonding. Our result is in good agreement to the work claimed by Scheithauer group [18, 44, 47] indicating that the Zr-OH group is required to create the strong Brønsted acid sites. This reveals that the crystalline zirconia support prepared from the solvothermal method also created Zr-OH bonding as well as amorphous zirconium oxide precursor. Based on the TON of catalyst the appreciable catalytic activity

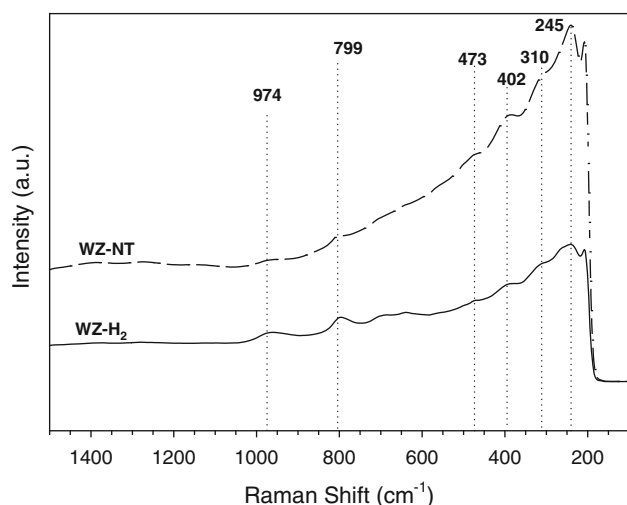
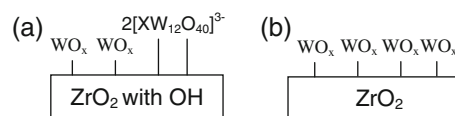


Fig. 4 Raman spectra of WZ-NT and WZ- H_2 catalysts



Scheme 1 Proposed catalytic active species presented in **a** WZ-NT and **b** WZ- H_2 catalyst

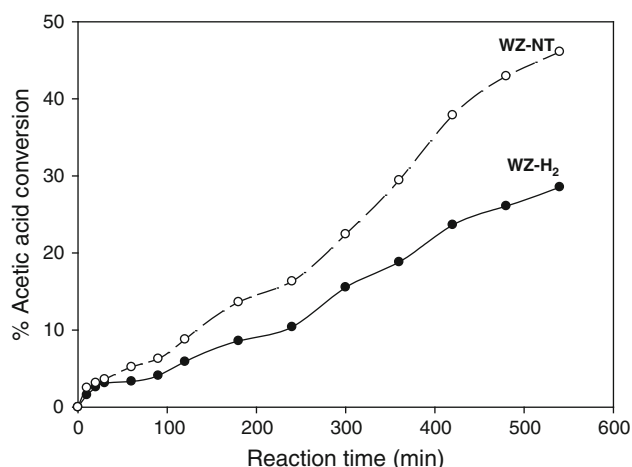


Fig. 5 Reaction profiles of acetic acid conversion using the different WZ catalysts

of both WZ-NT and WZ-H₂ were 100 times greater than that of the Amberlyst 15 as presented by Praserttham and Jongsomjit [1]. As known, the somewhat difference in response of water flow rate for the Amberlyst 15 versus WZ may have been caused by the presence of Lewis acid sites on WZ resulting in enhanced activity [6, 25, 26]. In addition, the WZ catalyst does not deactivate by leaching of active species in the liquid phase transesterification [8, 49], which is different from the SZ (sulfated zirconia) under similar condition. In order to prove that, the leaching experiment was also performed based on the procedure of Suwannakarn et al. [49]. It was found that the acetic acid conversion was less than 3%. This suggested that the leaching of active species in WZ catalyst did not occur for the WZ catalyst Fig. 5 upon the preparation used in this work [8, 12, 49].

4 Conclusions

In summary, the surface nature of zirconia was found to be crucial for determining the catalytic properties of WZ catalysts. The formation of Zr-heteropolyacid can be obtained from crystalline zirconia with Zr–OH bonding as presented in WZ-NT. This active species provided the strong Brønsted acid sites, which are essential for the esterification of dilute acetic acid and 1-heptanol. The Zr–OH bonding for WZ-H₂ was eliminated by the thermal treatment in the reduction atmosphere of the crystalline zirconia support allowing to the presence of only polytungstated domain.

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Ethylene-hexene copolymer derived from [t-butylfluorenylsilyl-amido] dimethyl titanium complex

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Abstract. The copolymers of ethylene and 1-hexene were prepared with half-metallocene titanium complex ([t-BuNSiMe₂Flu]TiMe₂) and modified methylaluminoxane (MMAO). The initial concentrations of 1-hexene were varied to investigate how the different amounts of comonomer affect on the catalytic activity of copolymerization system and microstructure of the copolymers. It has been found that this catalytic system was not active for hexene polymerization, however, it can be active when ethylene was introduced to perform ethylene-hexene copolymerization. As comonomer, 1-hexene provides positive comonomer effect on the system although very high concentration of 1-hexene was introduced. However, the microstructures of the obtained copolymers, which were examined by ¹³C-NMR need to be improved because with highly alternating sequence distribution of comonomer causing them losing some essential specific thermal properties.

Keywords: polymer synthesis, molecular engineering, metallocene, copolymer, LLDPE

1. Introduction

It is generally presumed that crystallinity of polymer plays an important role in determining the polymer properties, such as mechanical and thermal properties [1, 2]. We have known that, in synthesis of linear low-density polyethylene (LLDPE) by copolymerization of ethylene with α -olefins, the crystallinity depends mainly on the amount of α -olefin (comonomer) content in copolymer [3]. So, if the comonomer content can be controlled, properties of copolymer can be also altered. Appropriate crystallinity or comonomer content is varied depending on the application of polymer. The high comonomer content of copolymer has been commercially produced, named plastomers [1]. The advantages of plastomers are low density, high elongation, and low haze in film form. In order to obtain the plastomer derived from the metallocene

catalysts, the open structure of metallocene catalyst is crucial. Half-metallocenes and/or constrained geometry catalysts (CGCs) are subset of general metallocene catalyst, which pose the open structure because they have just one cyclopentadienyl ring (or their family, such as, indenyl or fluorenyl rings) bonded with the group IV transition metal leaving the opposite side of that ring large enough space for comonomer incorporation with less hindrance [4]. Therefore, plastomers or LLDPE with high comonomer content can be obtained with this type of catalyst.

As mentioned, comonomer contents are sensitive to many factors, such as the structure of catalyst, type of catalyst activators and the initial concentration of comonomer in the system. When considering the initial concentration, it has been found that the initial comonomer concentration not only affects

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directly on the comonomer contents, but it also affects on the catalytic activity of system [5, 6]. Therefore, in this present study the effect of the initial comonomer concentration in ethylene-1-hexene copolymerization with half-metallocene is investigated to determine both the catalytic performance and the specification of the obtained copolymers.

2. Experimental

2.1. Materials

All operations were manipulated under an argon atmosphere using glove box and/or standard Schlenk techniques. The $[t\text{-BuNSiMe}_2\text{Flu}]\text{TiMe}_2$ (Ti-complex) was synthesized according to the procedure described by Hagihara *et al.* [7]. Ethylene (polymerization grade) was obtained from the National Petrochemical Co. Ltd., Thailand. 1-Hexene ($\geq 97\%$) was purchased from Aldrich Chemical Company, Thailand and further purified by distilling over CaH_2 for 6 h. Modified methyl aluminoxane, MMAO $[(\text{Me}-\text{Al}-\text{O})_m(\text{i-Bu}-\text{Al}-\text{O})_n]$ having 1.86 M in toluene, was donated by Tosoh Akzo, Japan. Toluene (commercial grade) was donated by the Exxon Chemical, Thailand Co. Ltd. It was dried over dehydrated CaCl_2 and distilled over sodium/benzophenone.

2.2. Polymerization procedure

Ethylene/1-hexene copolymerization reaction was carried out in a 100 ml semibatch stainless steel autoclave reactor equipped with a magnetic stirrer. At first, the desired amounts of MMAO and the toluene were introduced into the reactor. The titanium complex in toluene ($10 \mu\text{mol}\cdot\text{ml}^{-1}$) was put into the reactor to make the $[\text{Al}]_{\text{MMAO}}/[\text{Ti}]_{\text{cat}} = 400$. Then, the reactor was immersed in liquid nitrogen. 1-hexene was added into the frozen reactor (to stop or prevent possible polymerization of 1-hexene). The reactor was heated up to the polymerization temperature at 343 K. The polymerization was started by feeding ethylene (0.018 moles) into the reactor. The ethylene pressure and reactor temperature were kept constant during the polymerization (pressure in reactor = 349 kPa (50 psi)). Due to the fixed ethylene consumption (at 0.018 moles), the polymerization time was defined as the time that all ethylene gas was totally consumed (the equivalent pressure drop of 42 kPa (6 psi) was observed). The

polymerization time was recorded to calculate the activity. The reaction was terminated by adding acidic methanol and the material was stirred for 30 min. After filtration, the copolymer obtained was washed with methanol and dried at room temperature.

2.3. ^{13}C -NMR spectroscopy

^{13}C -NMR spectroscopy was used to determine the α -olefin incorporation and copolymer microstructure. Chemical shifts were referenced internally to the CDCl_3 and calculated according to the method described by Randall [8]. Each sample solution was prepared by dissolving 50 mg of copolymer in 1,2,4-trichlorobenzene and CDCl_3 . ^{13}C -NMR spectra were taken at 333 K using a BRUKER AVANCE II 400 operating at 100 MHz with an acquisition time of 1.5 s and a delay time of 4 s.

2.4. Differential scanning calorimetry

The melting temperature of ethylene/1-octene copolymer products was determined with a Perkin-Elmer diamond DSC. The analyses were performed at the heating rate of $20^\circ\text{C}/\text{min}$ in the temperature range of $50\text{--}150^\circ\text{C}$. The heating cycle was run twice. In the first scan, samples were heated, and then cooled to room temperature. In the second scan, samples were reheated at the same rate, but only the results of the second scan were reported because the first scan was influenced by the mechanical and thermal history of samples.

3. Results and discussion

3.1. Reactivity of (co)monomer to catalyst

The catalytic activities based on polymer product are shown in Table 1. It can be seen that there is no catalytic activity for system conducted with only 1-hexene as monomer (**entry 1**). The opposite occurred on **entry 2** for the system that used only ethylene as monomer. It suggests that this half-metallocene catalyst ($[t\text{-BuNSiMe}_2\text{Flu}]\text{TiMe}_2$) is active for ethylene polymerization, but not for 1-hexene polymerization. This result agreed with the finding of Intaragamjon *et al.* [9], who reported that this catalyst cannot proceed 1-hexene polymerization under the specified condition. It has been known that ethylene is the most reactive olefin

Table 1. Activities of system with various monomer concentrations

Entry	Ethylene ^a [mol/l]	1-Hexene [mol/l]	Time [s]	Weight [g]	Activity ^b (kg polymer/mol Ti .h)
1	0.0	0.6	475	–	–
2	0.6	0.0	475	0.2468	187
3	0.6	0.3	500	1.0596	763
4	0.6	0.6	248	1.4030	2037
5	0.6	1.2	326	1.9241	2125

^aEthylene addition into the system^bCopolymerization condition: Ti = 10 μ mol, Al/Ti = 400, temperature = 343 K, 349 kPa (50 psi) of ethylene pressure was applied

[10], so it can react with itself for polymerization in the absence of any comonomer. Although 1-hexene was not reactive in its homopolymerization, it can be reacted in the system of copolymerization with ethylene (**entry 3–5**). Thus, this should be clarified in this finding that why 1-hexene was not active unless ethylene was introduced together in the system, even with the small amount of ethylene as seen for **entry 5**.

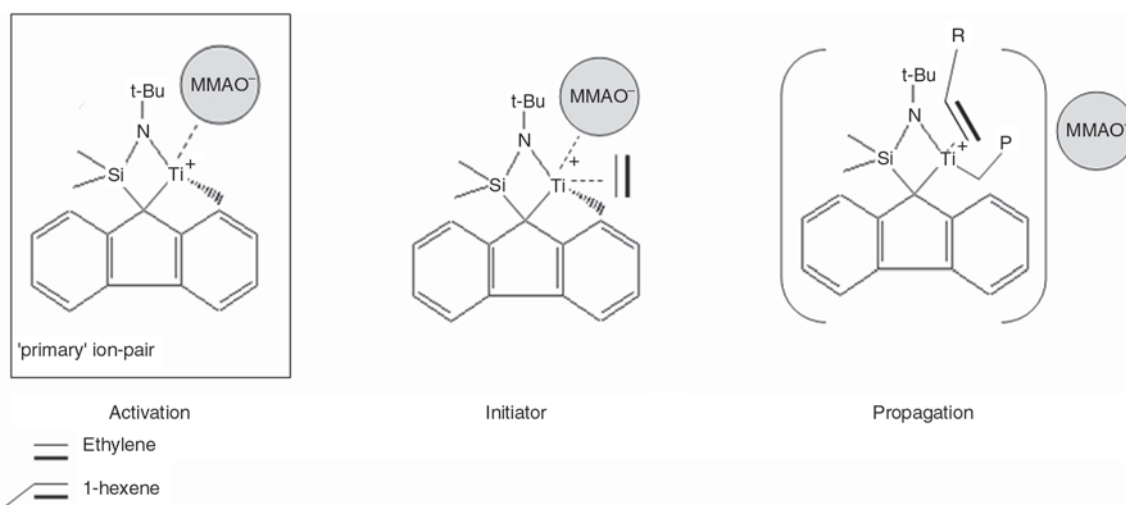
The mechanism of polymerization by metallocene catalyst system is reviewed here to explain the result. There are three main steps for completing the copolymerization (excluding chain transfer step), as shown in Figure 1 [10]. The first step is the ‘activation’ of metallocene catalyst typically achieving via contact with an appropriate cocatalyst species (MMAO in this case). The second is the ‘initiation’ of the polymerization occurring as a result of the displacement of the anion and coordination of the monomer in the primary complex. In our study, this step seems to be a problem for obtaining the 1-hexene polymerization, since the ion-pairs still stay in their coordinated tightly. Therefore, only the strong reactive monomer like ethylene is able to insert in this coordination, and

consequently displace the anion and make coordination with catalyst active site. This step can generate an available coordination site on the metal center, which provides high enough space for a large molecule, such as 1-hexene to coordinate with it in the next step. As the result, the final step that is the ‘propagation’ step will be the open competition between ethylene monomer and 1-hexene comonomer for insertion into the growing chain of polymer.

As describe above, for this catalytic system, if ethylene was not introduced into the system first, 1-hexene would not be reactive for this half-metallocene catalyst even open structure. However, in many cases, 1-hexene can perform polymerization by itself with some metallocenes such as $i\text{Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ and $\text{En}(\text{Ind})_2\text{ZrCl}_2$ [11] indicating that reactivities of α -olefin also depend on the catalyst structure [12].

3.2. Effect of the amount of 1-hexene on catalytic activity

In **entry 3–5**, introducing of 1-hexene into copolymerization enhanced catalytic activity higher than

**Figure 1.** Schematic representation of copolymerization mechanism

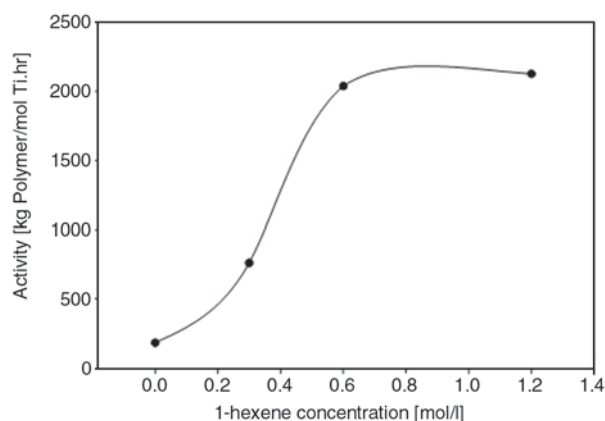


Figure 2. Activity profile with various 1-hexene concentrations

that of system without 1-hexene (**entry 2**). When the amounts of 1-hexene were increased, the catalytic activities were also increased. They increased pronouncedly when the amount of 1-hexene was raised from 0.3 to 0.6 mol/l. However, they gradually increased when the amount of 1-hexene was raised two times again from 0.6 to 1.2 mol/l. A comparison of activities is also shown in Figure 2. It can be explained that the first range of increasing is because of comonomer effect in copolymerization behavior [13]. The chain structure of 1-hexene can increase the gap between the cationic active species and counter anion more separately in propagation step (Figure 1). Then, the propagation rate of polymerization can be raised leading to enhancing the activity of copolymerization. However, at 1.2 mol/l of 1-hexene concentration (**entry 5**), the anticipated activity can not be attained. This is because high excess of 1-hexene obstructed active sites of catalyst from reacting with ethylene monomer, and consequently reduce rate of ethylene insertion into the chain of growing polymer. The explanation can be supported by polymerization time of **entry 5**, which was longer than that of **entry 4**. The longer polymerization time suggests that, in **entry 5**, the rate of ethylene consumption for polymerization was slower than that of **entry 4**.

Although the rate of ethylene consumption in **entry 4** was faster, activity or productivity of **entry 5** was higher. This is because initial concentration of 1-hexene of **entry 5** was higher then it can produce more product than **entry 4** did resulting in high catalytic activity for the system.

3.3. Effect of the amount of 1-hexene on microstructure of copolymers

As seen in Table 2, the comonomer incorporations apparently increased with increasing the amount of 1-hexene in copolymerization. In this copolymerization process, which fixed the amount of ethylene addition and kept ethylene pressure constant during copolymerization, the incorporation of 1-hexene can be increased by two primary reasons. One is that enhancing the reactivity of 1-hexene or two, diminishing the reactivity of ethylene. It can be seen from Table 2 that reactivities of ethylene decreased dramatically with increasing the concentration of 1-hexene in the system while reactivities of 1-hexene just slightly increased. So, it can be concluded that the initial concentrations of 1-hexene in the system have more effect on the reactivity of ethylene than itself. The increase of 1-hexene reactivity enables it to still incorporate continuously into the growing chain even at high concentration. The open structure of half-metallocene catalyst is one of the important factors that retains high reactivity of 1-hexene and encourages high comonomer incorporation. As compared with the works done by our group previously with normal metallocene, it has been found that with the same initial comonomer concentration in copolymerization, the obtained copolymer from those studies exhibited much lower comonomer incorporation than in this study [14, 15].

On account of the fact that the uniform comonomer incorporation is the key feature for producing low-density plastomer, which exhibited plastic and elas-

Table 2. Comonomer incorporation and the reactivity ratios

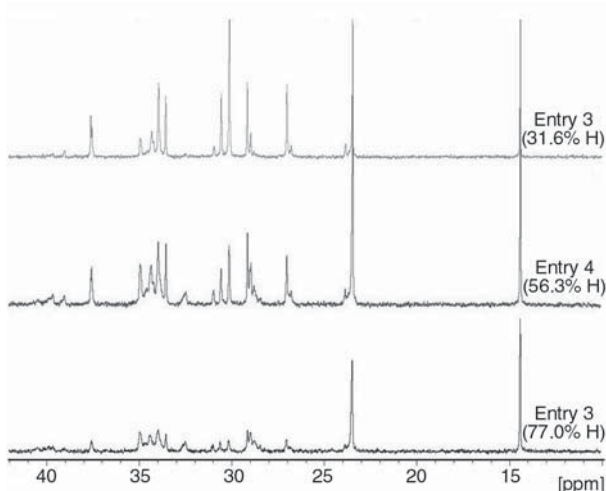
Entry	Ethylene [mol/l]	1-Hexene [mol/l]	Incorporation ^a		Reactivity ^b		
			E [mol %]	H [mol %]	r_E	r_H	$r_E r_H$
3	0.6	0.3	68.4	31.6	1.121	0.658	0.737
4	0.6	0.6	43.7	56.3	0.797	0.738	0.588
5	0.6	1.2	23.0	77.0	0.621	0.784	0.487

^aExamined by ¹³C-NMR by Randall method [8]

^bRelative comonomer reactivities (r_E for ethylene and r_H for 1-hexene) calculated by $r_E = 2[EE]/[EC]X$, $r_H = 2X[CC]/[EC]$, $[EE] = [EEE] + 0.5[CEE]$, $[CC] = [CCC] + 0.5[ECC]$, $[EC] = [CEC] + 0.5[C EE] + [ECE] + 0.5[ECC]$

Table 3. Triad distribution of copolymer obtained from ^{13}C -NMR

Entry	Ethylene [mol/l]	1-Hexene [mol/l]	EEE	EEH	HEH	EHE	EHH	HHH
3	0.6	0.3	0.345	0.292	0.048	0.172	0.144	0.000
4	0.6	0.6	0.091	0.270	0.076	0.185	0.339	0.039
5	0.6	1.2	0.015	0.130	0.085	0.154	0.424	0.192

**Figure 3.** ^{13}C -NMR spectra of copolymers

tomeric behavior [16], the distribution of comonomer in the copolymers needs to be concerned in order to obtain plastomers with desired specification. The triad distribution for all copolymers obtained from ^{13}C -NMR is shown in Table 3. Triad block of comonomer (HHH) was detected in samples having 1-hexene incorporation above 31.6% (**entry 4, 5**). It was also noticed from Figure 3, which showed ^{13}C -NMR spectrum of the copolymers that the peaks between 39.5 and 42 ppm (proportional to the HHH triad) occurred obviously in the copolymer from **entry 4** and **5**. Nevertheless, the number of HHH triad was not converted directly from the area under these peaks. There are other peaks, which are more pronounced in the calculation. Therefore, the larger area of these peaks of **entry 4** than **entry 5** did not mean that **entry 4** had more HHH triad than **entry 5**.

The presence of HHH triad can imply that the good distribution of comonomer throughout the copolymer chain was interrupted at high incorporation of comonomer. Although the copolymers with high 1-hexene incorporation contain the block of comonomer, they are still not the block copolymer. It can be observed from the product of reactivity ratio (r_{EH}), which is one of the parameters that can identify types of copolymer. A value $r_{EH} > 1$ indicates a block copolymer structure and $r_{EH} < 1$

reveals an alternating copolymer structure. Therefore, all the obtained copolymers are alternating copolymers having the r_{EH} value being lower than 1. Once the alternating copolymers were obtained, it means the comonomers in their chain are distributed moderately well along the backbone, then shortening the average backbone sequence length for crystallization and therefore low crystallinity, including low density, would be gained. Thus, with these properties, the obtained copolymers are in closing proximity to be low-density plastomer. However, these copolymers might not meet all properties required for the use in plastic industry because they probably lost completely the thermal properties.

As a result of the fact that disadvantages of alternating copolymer, which have been found by Hung *et al.* [17] that the polymer with a highly alternating sequence distribution did not exhibit any melting behavior. Based on the result, when the incorporations of comonomers increased, the obtained polymer tended to exhibit more highly alternating copolymer structure ($r_{EH} < 1$). Therefore, they might lose the melting behavior at high level of 1-hexene incorporation. To prove that, melting temperatures of the obtained polymers were investigated by differential scanning calorimetry (DSC). From the investigation, it was found that only the sample from **entry 2**, which is the polyethylene sample, has the melting temperature (130°C) and the remaining samples cannot be found the melting temperatures. Thus, the losses of thermal properties existed in all obtained copolymers even the one that had low comonomer content (**entry 3**, 31.6%).

Copolymers were formed the gel-like structure as seen in Figure 4 when the 1-hexene was introduced into the system, especially at the high level of incorporation. With this structure, it is obviously shown the character of amorphous material. Therefore, it accords with the results from ^{13}C -NMR and DSC that the obtained copolymers should not have the melting temperature.

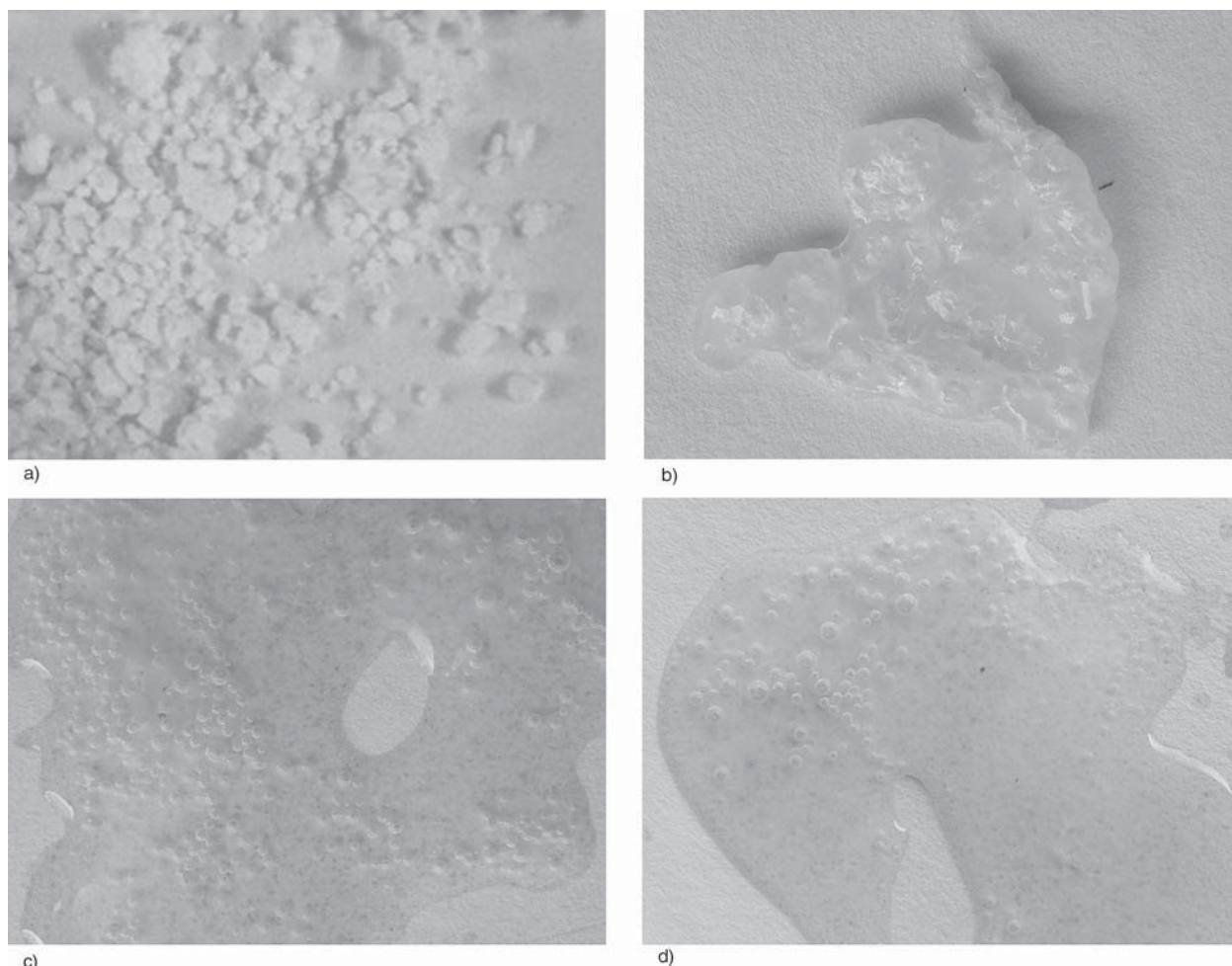


Figure 4. Digital photograph of copolymer with various 1-hexene contents a) 0%, b) 31.6%, c) 56.3% and d) 77.0%

4. Conclusions

It was found that the positive comonomer effect occurred even though a very high concentration of 1-hexene that was introduced into the system. However, the microstructures of the obtained copolymer examined by ^{13}C -NMR need to be improved because the highly alternating sequence distributions of copolymer cause the loss of essential specific thermal properties.

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Study on Solvent/Alkoxide Molar Ratios on Synthesis Zirconia Nanoparticles for Tungstated Zirconia Catalysts Over Esterification

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Abstract A series of nanocrystal zirconia samples were synthesized, characterized and studied for the esterification reaction. The results showed that the solvothermal method under different solvent/alkoxide molar ratios led to remarkable effect on the amount of carbon residue remained on the surface of catalysts resulting in the difference in proton species-support interaction behavior. Moreover, the esterification activity of W/ZrO_2 varied distinctly with the solvothermal synthesis condition of nanocrystal zirconia.

Keywords W/ZrO_2 · Solvothermal synthesis · Solvent content · Carbon residue · Esterification

1 Introduction

A large number of industrially important reactions are catalyzed by solid acids. To improve their performance, a detailed characterization of these catalysts is important. Specifically, a systematic study of the development of acid sites in relation to the nature of the surface structure is of particular interest. Solid acids catalysts of the type WO_x/ZrO_2 have attracted much interest recently due to their structural feature which can present strong acidic sites, and thus are active for isomerization, alkylation and esterification [1–6].

The structural feature of the WO_x/ZrO_2 catalysts have been studied [7–12] and was showed that the active species-support interaction plays an important role in controlling the active phase features and in affecting the support properties. Some authors suggest that the catalytic activity is associated with interconnecting amorphous WO_x species on the surface of tetragonal zirconia. The creation of strong acidic centers appears to require the presence of WO_x clusters in the presence of a significant proportion of tetragonal zirconium oxide (ZrO_2) [10, 13]. Several works have shown that the catalytic properties of the WO_x/ZrO_2 are strongly affected by every step of the preparation including the choice of the synthesis method and tungsten loading. The main influences of the preparation method are on: (i) the type of the active species formed; (ii) the dispersion of the active species; (iii) the acidity of the catalyst; (iv) the different types of phases formed and (v) the surface area. Synthesis methods, such as impregnation, co-impregnation, hydrothermal, sol-gel, and solvothermal, have been widely studied to optimize the preparation of such catalysts with properties being appropriate for different purposes [14–17]. Among these methods, the most used one for the preparation of pure tetragonal zirconia phase is the solvothermal method. In this case, the procedure consists of impregnation of crystal zirconium oxide with a solution containing tungsten precursor [18]. After the calcination, the tungsten species formed were composed of isolated surface monotungstates and/or polymeric surface polytungstates species (WO_x) and WO_3 crystallites [19]. Previous studies have emphasized on the amounts of residual carbon remained the surface of catalysts certain characteristics of the degree of interaction between the zirconia and adsorbed species [20]. It revealed that ZrO_2 particles prepared in 1,4-butanediol (ZrO_2 -BG) have the lowest amounts of residual carbon on the surface of

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catalysts leading to enhanced activity for tungstated zirconia catalyst.

In the present research, we synthesized the nanocrystalline zirconia by the solvothermal method under different solvent (glycol)/alkoxide molar ratios and investigated the effects of the properties of zirconia obtained on the esterification performances of W/ZrO_2 . It was confirmed that carbon residue present on the surface of catalysts affects the activity for tungstated zirconia catalyst in acetic acid esterification reaction.

2 Experimental Section

2.1 W/ZrO_2 Catalyst Synthesis

W/ZrO_2 samples were prepared by the adsorption of a W precursor on the surface of nanocrystalline zirconia (ZrO_2). First the zirconia support was prepared by the solvothermal method of zirconium tetra-*n*-butoxide 80 wt% solution in 1-butanol [$Zr(OCH_2CH_2CH_2CH_3)_4$, Aldrich] and 1,4-butanediol [$HO(CH_2)_4OH$, Sigma-Aldrich, 99%]. A desired amount of an alkoxide was suspended in 100 mL of 1,4-butanediol in a glass vessel, and then placed in a 300-mL autoclave filled with 30 mL of the same solvent. The autoclave was completely sealed and purged with nitrogen. The mixture was heated to the desired temperature at a constant rate of $2.5\text{ }^{\circ}\text{C min}^{-1}$ and held at that temperature for 2 h. After the autoclave was cooled, the resulting powder was washed repeatedly with methanol by centrifugation, and then air-dried at room temperature. The products were then air-dried and used without further calcinations. The molar ratios of solvent/alkoxide used in this work were ranged from 12 to 29.

A series of samples was prepared by the incipient wetness impregnation method using tungsten(VI) chloride (WCl_6 , Aldrich, 99.9%) sufficient for yield materials having 15 wt% of W loading. The catalysts were dried at $110\text{ }^{\circ}\text{C}$ for 12 h and finally calcined at $500\text{ }^{\circ}\text{C}$ in air for 3 h [4].

Samples are designated as ZrO_2 -*x* and W/ZrO_2 -*x*, where *x* refers to the molar ratios of solvent/alkoxide.

2.2 X-Ray Diffraction

X-ray powder diffraction spectra were recorded using a Siemens (D5000, Germany) powder diffractometer with a copper anode ($Cu\text{ K}\alpha$, $\lambda = 0.15418\text{ nm}$) and a scanning rate of $0.04^{\circ}\text{ s}^{-1}$. The crystalline planes of phases *t*- ZrO_2 and *m*- ZrO_2 were indexed following the Joint Committee on Powder Diffraction Standards (JCPDS) cards and the crystallite size was calculated from the Scherrer equation.

2.3 BET Surface Area

Nitrogen adsorption was measured at $-196\text{ }^{\circ}\text{C}$ with an automatic adsorptiometer (Micromeritics ASAP 2020, USA). The samples were pretreated at $300\text{ }^{\circ}\text{C}$ for 3 h under vacuum. The surface areas were determined from adsorption values for relative pressures (P/P_0) ranging from 0.1 to 1.0 using the Brunauer–Emmett–Teller (BET) method.

2.4 Scanning Electron Microscope

Surface morphology of the samples was observed on Hitachi S-3400N (Japan) scanning electron microscope (SEM) with an acceleration voltage of 15 kV. Catalyst samples were gold coated prior to scanning.

2.5 Transmission Electron Micrographs

The TEM measurement was obtained using a JEOL JEM-2010 (Japan) transmission electron microscope. The samples were supported on carbon-coated copper grids for the experiment.

2.6 Thermogravimetric Analysis

The thermogravimetric (TG) analyses were performed on a TA Instruments SDT Q 600 analyzer (USA). The samples of 10–20 mg and a temperature range between 30 to $800\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$ were used in the operation with N_2 UHP carrier gas.

2.7 X-Ray Photoelectron Spectroscopy

The XPS measurement was carried out using an AMICUS photoelectron spectrometer (UK) equipped with an $Mg\text{ K}\alpha$ X-ray as a primary excitation and KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step at a pass energy of 75 kV. The background pressure during the spectra accumulation was typically 10^{-6} Pa . Detailed spectral scans were taken over Zr 3d, O 1s, W 4f, C 1s and Ag 3d regions. The binding energy scale of the spectra was calibrated to the silver Ag 3d_{5/2} peak at the energy of 368.2 eV [21].

2.8 Acidity Measurements

The number of acid sites was also estimated by using a method involving an aqueous ion-exchange step, in which 0.2 g of catalyst was added to 10 mL of a 3.42 M aqueous solution of NaCl under stirring. The exchange ions between H^+ of catalyst and Na^+ in the solution were carried out for 30 h at room temperature; the liquid was filtered off and titrated with a 0.05 N aqueous NaOH solution.

The endpoint for titration was determined using a pH meter (pH $\sim$ 7) and corroborated using pH paper [4, 22].

2.9 Catalytic Activity

The esterification of acetic acid with methanol has been used as a probe reaction for studying the activity of the catalysts. The reaction was carried out in liquid phase batch reactor. The WZ catalyst taken was 2 wt% of acetic acid, and acetic acid and methanol were taken in 1:3 molar ratio. In a typical procedure, a 250-mL round bottom flask equipped with a water condenser and magnetic stirrer was kept in a constant temperature of oil bath. The reaction was carried out at atmospheric pressure at 60 °C. Sample was withdrawn periodically from the reactor, quenched to room temperature, and centrifuged in order to separate the solid catalyst from product to prevent further reaction. Concentration of reacted samples was determined using a SHIMADZU gas chromatograph (GC-14B) equipped with Chrompack SE52 column and flame ionization detector. UHP N₂ was used as the carrier gas.

3 Results and Discussion

The XRD patterns are shown in Fig. 1. It reveals that zirconia in the samples existed mainly in the form of tetragonal phase (*t*-ZrO₂) and only very few percentages of monoclinic zirconia (*m*-ZrO₂) were detected in ZrO₂-15 and ZrO₂-12 [23]. The average crystallite sizes calculated from the XRD line broadening using the Scherrer equation and the BET surface areas of the zirconia are reported in Table 1. The average crystallite sizes of zirconia were approximately 3.4–4.0 nm. Within experimental error, there was no significant difference in BET surface areas

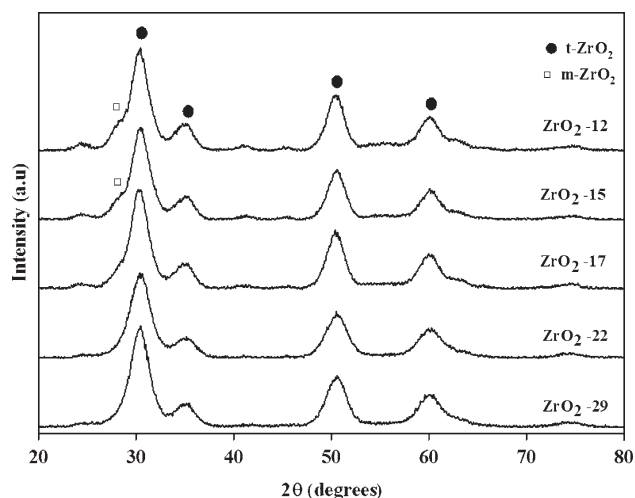


Fig. 1 XRD patterns of the ZrO₂

Table 1 Textural characterization of zirconia supports

Sample	Crystallite size ^a (nm)	BET surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
ZrO ₂ -29	3.8	171	2.60	0.10
ZrO ₂ -22	3.4	170	2.52	0.09
ZrO ₂ -17	3.9	186	2.64	0.17
ZrO ₂ -15	3.8	187	2.68	0.18
ZrO ₂ -12	4.0	185	2.72	0.19

^a Calculated from XRD measurement based on Scherrer equation

and the crystallite sizes of the zirconia prepared in different solvent/alkoxide molar ratios (different ZNB concentrations). To check accuracy of the crystal size obtained from the XRD analysis, TEM photographs of products were also taken in comparison. Figure 2 shows an agglomeration of crystals with an average diameter of 4.4 nm in ZrO₂-17. Since the crystal sizes from TEM and X-ray analysis are in good agreement, it has been concluded that each primary particles of the obtained products are single crystals of zirconia. These results were found to be in agreement with our previous work [24].

Typical SEM micrographs of zirconia samples prepared in 1,4-butanediol with different molar ratios of solvent/alkoxide are shown in Fig. 3a–e. The powders have a spherical shape and a dense mass and seem to be formed by aggregations of primary particles. The SEM photograph shows these secondary particles as separate microspheres. Interestingly, the lower solvent/alkoxide ratios (higher the initial ZNB concentration), the larger the size of the

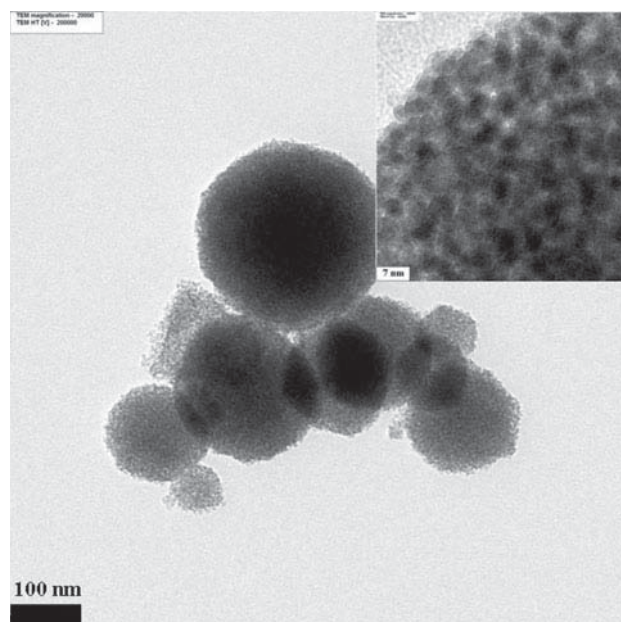


Fig. 2 TEM image of ZrO₂-17

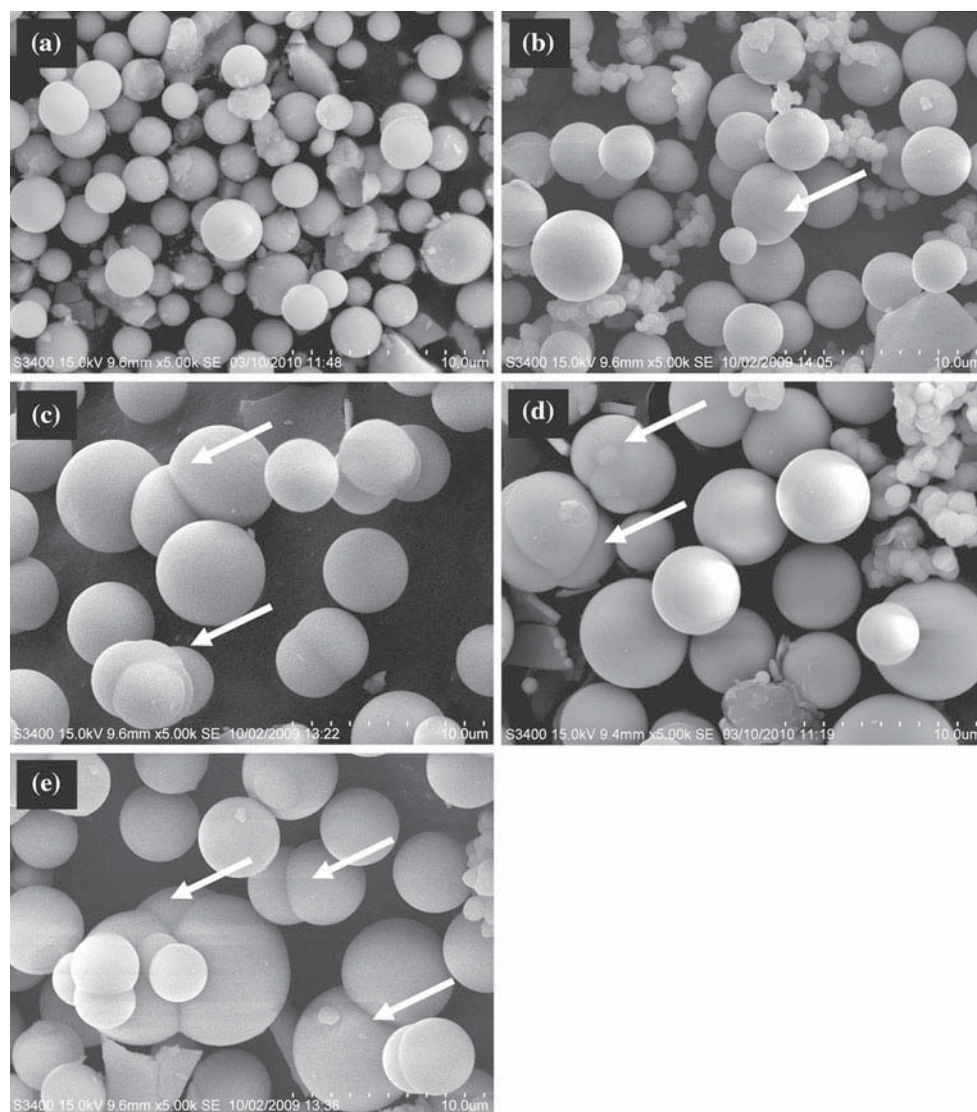


Fig. 3 SEM photographs of products synthesized in 1,4 butanediol at 250 °C of **a** ZrO₂-29, **b** ZrO₂-22, **c** ZrO₂-17, **d** ZrO₂-15 and **e** ZrO₂-12

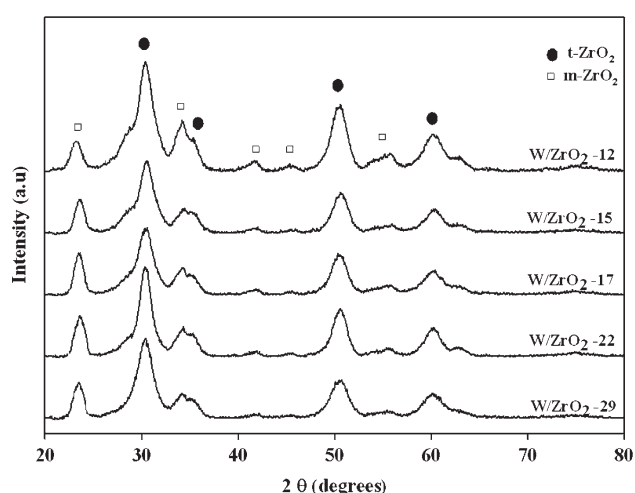
secondary particle. Furthermore, we can see boundaries of small microspheres that agglomerated to form larger secondary particles. These boundaries are indicated by arrows in Fig. 3. Increasing solvent/alkoxide ratios decreases mean microsphere diameter while reducing sharply the number of small microspheres.

Table 2, compares the catalytic properties of various zirconia supported tungsten catalysts. In this study, the zirconia was impregnated with 15 wt% of tungsten and calcined in air at 500 °C for 3 h. In general, the penetration of tungsten species into the pore of ZrO₂ support could reduce the surface area of the tungstated zirconia catalysts. This loss of surface area is significantly inhibited by the presence of WO_x species [4] or the emergence of monoclinic zirconia (*m*-ZrO₂). In order to estimate the theoretical nominal W surface densities, W/ZrO₂ surface area and

amount of tungsten loading were used [25]. It was found that the W surface coverage of all catalysts were presented as the growing surface monotungstated domain (approximately 3.6–4.0 W/nm²) [7]. It would appear that the surface area and particle size of the catalyst particles were not affected by solvent/alkoxide ratio since no physical changes were observed. The X-ray diffraction patterns of the zirconia-supported tungsten catalysts are shown in Fig. 4. The increased calcination temperature was also allowing to present a fraction of *m*-ZrO₂. It should be noted that the XRD peak at ca. 24.3° for all samples was assigned to the monoclinic zirconia (not WO_x crystallites) [26–28]. The results were found to be in agreement with the work previously reported by our group, the catalysts did not show diffraction peaks at 2θ = 23.2, 23.6 and 24.48 and did not show Raman bands at 720 and 807 cm⁻¹ that

Table 2 Physicochemical properties of W/ZrO₂ catalysts

Sample	Crystallite size ^a (nm)	BET surface area (m ² /g)	W surface density ^b (W atom/nm ²)	Surface acidity ^c (μmol/g)	C atomic concentration ^d (%)
W/ZrO ₂ -29	4.5	123	4.0	88	20.03
W/ZrO ₂ -22	4.7	128	3.8	94	16.30
W/ZrO ₂ -17	4.4	134	3.7	112	14.63
W/ZrO ₂ -15	4.6	135	3.6	120	13.32
W/ZrO ₂ -12	4.4	136	3.6	128	12.08

^a Calculated from XRD measurement based on Scherrer equation^b Calculated from the equation [25] Surface density = $\frac{\{\text{Promoter loading (\%)/100}\} \times 6.023 \times 10^{23}}{\text{Formula weight of promoter} \times \text{BET surface area (m}^2 \text{ g}^{-1}) \times 10^{18}}$ ^c Measured by ion-exchange and titration with 0.05 N NaOH^d Measured from XPS measurement**Fig. 4** XRD patterns for W/ZrO₂ calcined at 500 °C for 3 h

are characteristic of WO₃ [18, 20, 29]. No diffraction peaks of WO₃ crystallites were observed for all samples, indicating that tungsten oxide was well dispersed on zirconia.

The acid site concentrations as measured by ion-exchange titration are also listed in Table 2. It was found that they are in the range of ca. 88, 94, 112, 120 and 128 μmol/g for W/ZrO₂-29, W/ZrO₂-22, W/ZrO₂-17, W/ZrO₂-15 and W/ZrO₂-12 samples, respectively. The number of acid sites increases in parallel with the decreased solvent/alkoxide molar ratio. Probably as a result of the residue carbon deposit on the surface of catalyst. The

amounts of residue carbon on the surface of catalysts were characterized by XPS, as shown in Table 3. The C 1s envelopes were analyzed and peak-fitted after subtraction of a Shirley background using a Gaussian peak shapes is shown in Fig. 5. In this deconvolution operation, the FWHM value adopted for all the C 1s lines were not higher than 2.4 eV. High residual carbon concentrations are apparently evident for the W/ZrO₂-29. It can be seen that when the solvent ratio was decreased from 29 to 12, the carbon concentration decreased ca. 40%. These results indicate a more pronounced effect of solvent ratio on the carbon residual concentration and the acid site concentration of tungstated zirconia catalyst.

The esterification of acetic acid with methanol was carried out over the catalysts of W/ZrO₂-29, W/ZrO₂-22, W/ZrO₂-17, W/ZrO₂-15, and W/ZrO₂-12 at 60 °C; the conversions of acetic acid after 6 h of time on stream are shown as a function of time in Fig. 6. The figure shows that the W/ZrO₂ catalysts are quite effective for the reaction, the W/ZrO₂-12 catalyst showed especially high activities for the esterification of acetic acid. This is due to the highest acidity present as observed from acid–base titration techniques (Table 2). It is interesting to note that the ratio of solvent/glycol of the zirconia support synthesis has an influence on the catalytic activity of the tungstated zirconia catalysts. It is found that the conversion of acetic acid decreases with increasing the solvent/glycol ratio from 12 to 29 as shown in Fig. 6. This is mainly due to the fact that

Table 3 C 1s XPS results

Sample	Position BE (eV)	FWHM (eV)	Raw area (CPS)	R ²	Carbon concentration	
					Atomic%	Mass%
W/ZrO ₂ -29	285.063	2.180	2643.5	0.98859	20.03	6.0
W/ZrO ₂ -22	284.832	2.306	2340.9	0.97740	16.30	4.7
W/ZrO ₂ -17	284.708	2.192	1927.2	0.98559	14.63	4.5
W/ZrO ₂ -15	284.849	2.162	1870.1	0.98092	13.32	3.9
W/ZrO ₂ -12	285.052	2.122	1549.9	0.98396	12.08	3.6

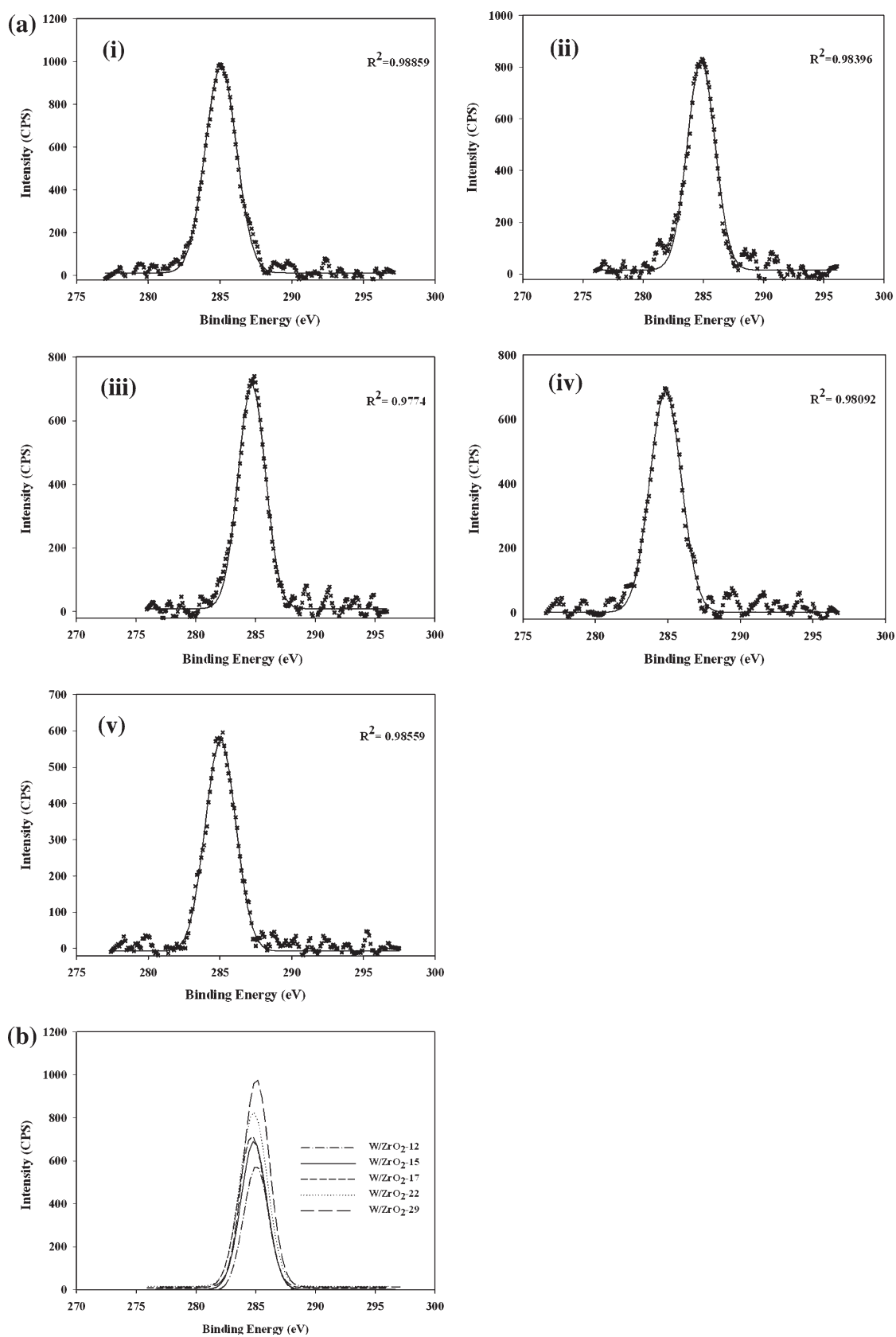


Fig. 5 **a** C 1s XPS normalized spectra of a surface of (i) W/ZrO₂-29, (ii) W/ZrO₂-22, (iii) W/ZrO₂-17, (iv) W/ZrO₂-15 and (v) W/ZrO₂-12. **b** Evolution of C 1s XPS spectrum of a surface of various tungstated zirconia catalysts

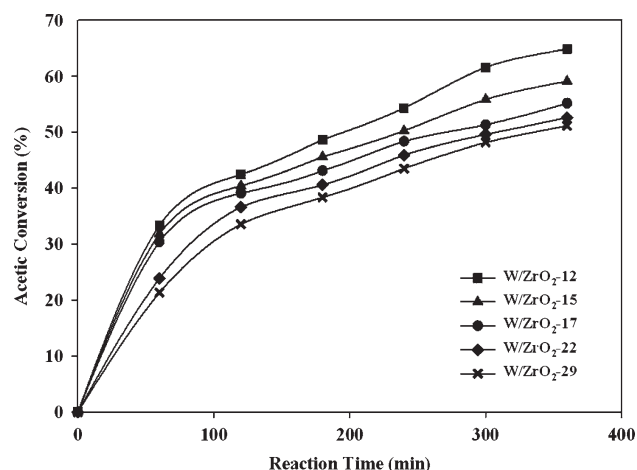


Fig. 6 Catalytic activity on the different W/ZrO₂ catalysts

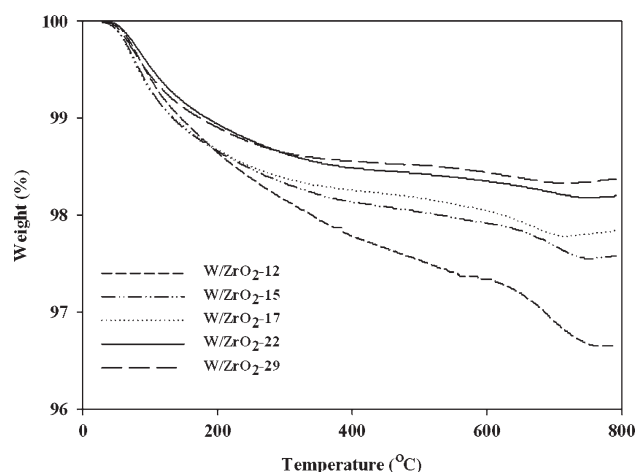
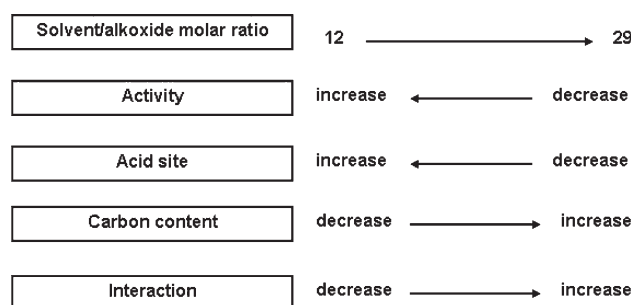


Fig. 7 TGA profiles of tungsten oxide on different supports

W/ZrO₂-29 catalyst has the maximum residue carbon on the surface (Table 3 and Fig. 5). The results clearly show, in agreement with previous reports [20], an increased carbon residue on the surface of catalysts. The acidity of the solids after calcination at 500 °C was affected by the residue carbon deposition on the surface of the catalysts. One of the possible reasons is that the interaction between the support and the dispersed oxide species. In order to prove the interaction between the tungsten oxide and support, TGA measurement was performed. The TGA can provide the useful information on the degree of interaction for adsorbed species bound to support in terms of weight loss and removal temperature [20, 30–33]. The TGA profiles for all catalysts are shown in Fig. 7. We observed that the weight losses of samples were in the order of W/ZrO₂-12 (3.3%) > W/ZrO₂-15 (2.4%) > W/ZrO₂-17 (2.2%) > W/ZrO₂-22 (1.8%) > W/ZrO₂-29 (1.6%). This indicated that adsorbed species present on ZrO₂-29 had the strongest interaction among other supports, resulted in the lowest



Scheme 1 Relationship between solvent/alkoxide molar ratios and other parameters

activity obtained. In addition, the relationship between the solvent/alkoxide ratios and other parameters is summarized as shown in Scheme 1.

4 Conclusions

The liquid-phase esterification of acetic acid with methanol at 60 °C was investigated to characterize the effect of solvent/alkoxide molar ratios on synthesis nanocrystal zirconia support on the esterification performances of W/ZrO₂. The catalytic activity of W/ZrO₂-12, zirconia support prepared by solvothermal method with the molar ratio of solvent/alkoxide = 12 showed highest surface acidity consequently having the highest activity. It can be concluded that the molar ratios of solvent/alkoxide remarkably affect the amount of carbon residue on the surface of catalysts resulting in the difference in acidity of catalyst.

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The influence of Si-modified TiO₂ on the activity of Ag/TiO₂ in CO oxidation

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ABSTRACT

Nanocrystalline TiO₂ and Si-modified TiO₂ with Si/Ti ratios 0.01, 0.05, 0.1, and 0.3 were prepared by the solvothermal method and employed as the supports for Ag/TiO₂ catalysts for CO oxidation reaction. The incorporation of Si into the TiO₂ lattice in the form of Ti–O–Si as revealed by FT-IR results could inhibit the agglomeration of TiO₂ crystallites, resulting in an increase of both surface area and metal dispersion. However, there existed an optimum content of Si/Ti at ca. 0.05–0.1 which resulted in an improved catalytic activity of Ag/TiO₂ in CO oxidation. Based on the O₂-temperature program desorption (O₂-TPD) results, the catalysts with appropriate amounts of Si/Ti exhibited higher amount of O₂ adsorption and much lower desorption temperature. It is suggested that the presence of Ti–O–Si promoted the formation of active oxygen species and increased the mobility of lattice oxygen so that the catalytic activity was enhanced. There was no improvement in CO oxidation activity of the Ag/TiO₂ catalyst when the Si/Ti was further increased to 0.3 due probably to the formation of amorphous SiO₂ instead of the Ti–O–Si bond.

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1. Introduction

The main purpose of support modification is generally to obtain high dispersion of metal catalyst or high active sites for catalytic reaction. Support modification usually brings about changes in surface properties of the support such as surface area and interaction between metal particles and support, which are a crucial factor affecting catalytic activity of the metal. The modification of support with trace element has been investigated widely by many researchers. This method can result in changes in surface chemistry, crystal structure and size, and crystal defects of support. For TiO₂ support, various doping elements have been studied including silicon [1–6] lanthanum [7,8], yttrium [9–11], zirconium [12–14], etc. The incorporation of trace element has shown to increase both surface area and thermal stability of the support.

It is well known that titanium dioxide (TiO₂) is reducible metal oxide that stronger interacts with group VIII noble metals than other metal oxides such as SiO₂, Al₂O₃, and MgO [15–19]. For this reason, titanium dioxide has attracted much attention for the application as noble metal catalyst support in many reactions. CO oxidation is one of the reactions that have been frequently investigated using TiO₂ as the support. Nevertheless, only a few studies have reported about the modification of TiO₂ with trace

elements for application as catalyst support in CO oxidation reaction. For examples, Tai et al. [20] have shown that modification of TiO₂ aerogel support with silica-coating improved the catalytic activity of Au/TiO₂ compared to that on pure TiO₂ support. Yu et al. [8] reported that doping of La in TiO₂ support during the sol-gel synthesis also enhanced the catalytic activity of Au/TiO₂ in CO oxidation.

In this work, the effect of Si doping in TiO₂ support synthesized by solvothermal method on the physicochemical properties of TiO₂ and the catalytic activities of Ag/TiO₂ catalysts in the CO oxidation reaction were investigated. The catalysts were also characterized by X-ray diffraction (XRD), Fourier transformed spectroscopy (FT-IR), temperature programmed desorption of oxygen (O₂-TPD), and pulse chemisorption.

2. Experimental

2.1. Preparation of TiO₂ and Si-modified TiO₂

The TiO₂ nanoparticles were prepared by the solvothermal method according to that of Ref. [21]. Titanium (IV) *n*-butoxide (TNB) (97%, Aldrich) and 1,4-butanediol (Aldrich) were used as TiO₂ precursor and organic solvent, respectively. Firstly, 25 g of TNB was dissolved in 100 cm³ of 1,4-butanediol. The solution was mixed in the test tube and placed in 300 cm³ autoclave. Additional 1,4-butanediol, with a volume of about 30 cm³, was filled into the gap between the test tube and the autoclave wall. The nitrogen gas was purged into the autoclave reactor before heating up to 320 °C

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at a rate of 2.5 °C/min and held constant at that temperature for 4 h. The Si-modified TiO₂ was prepared by addition of a certain amount of tetraethylorthosilicate (TEOS, Aldrich) into the mixed solution of TNB and 1,4-butanediol before setting up in the autoclave. The molar ratios of Si/Ti were varied in the range of 0.01–0.3. After cooling naturally to room temperature, the products were repeatedly washed with methanol and dried in air.

2.2. Preparation of Ag/TiO₂ catalysts

The obtained TiO₂ powder was used as support for preparation of Ag/TiO₂ catalyst. A certain amount of AgNO₃ was dissolved in deionized water and loaded on the support by the incipient wetness impregnation method. After impregnation, the samples were dried at room temperature for 6 h and then at 110 °C overnight in an oven. The obtained samples were calcined in air at 450 °C for 3 h. The metal content was maintained at 10 at.%Ag with respect to the atomic weight of the TiO₂ support. The series of catalysts are denoted by their atomic percentages of metal loading and the silicon content in the TiO₂ supports. For example, 10%Ag/TiO₂-0.01Si is referred to the catalyst containing 10 at.%Ag on the Si-modified TiO₂ with the molar ratio of Si/Ti 0.01.

2.3. Catalyst characterization

The XRD analysis was performed using the SIEMENS D5000 diffractometer with Cu K_α radiation. The crystallite size and crystalline phase of Si-modified TiO₂ were estimated by the Scherrer equation. The XRD patterns were collected at a rate of 2.4° min⁻¹ in the range of 2θ = 20–80°. The particle sizes of Si-modified TiO₂ were investigated by transmission electron microscopy (TEM) with a Philips CM100 microscope. The specific surface area of samples was determined by the Brunauer–Emmet–Teller (BET) method using N₂ adsorption at 77 K in a Micromeritics ASAP 2020 instrument. The FT-IR spectra were collected at room temperature using a NICOLET 6700 spectrometer in the range of 400–4000 cm⁻¹ with 4 cm⁻¹ resolution by the KBr technique. The sample and KBr were dried at 110 °C for 24 h before analysis. The samples were measured in a controlled humidity room. The amount of metal active sites for Ag/TiO₂ catalysts was determined using N₂O pulse chemisorption according to the method described previously by our group [22]. Approximately 100 mg of the catalyst sample was reduced in hydrogen flow (50 cm³/min) at 200 °C. After that the temperature was cooled down to 150 °C in He stream and a certain amount of N₂O was injected. The N₂O was analyzed by TCD gas chromatography using a packed Porapak N column. The metal active site of the Ag/TiO₂ catalyst was calculated assuming a reaction stoichiometry of two Ag per oxygen atom.

The O₂-TPD experiment was performed in order to study the characteristics of oxygen adsorption and desorption on the catalyst surface. This method was adapted from Yu et al. [8]. Approximately, 0.1 g of the catalyst was reduced at 200 °C in hydrogen flow (50 cm³/min) for 1 h. The temperature was then cooled down to 30 °C in He stream (30 cm³/min) and followed by oxygen adsorption at 30 °C for 1 h with a flow of oxygen (30 cm³/min). The physically adsorbed oxygen on the catalyst surface was swept out with He stream until no signal of oxygen could be detected and then the temperature was ramped with a heating rate of 10 °C/min to 600 °C. The oxygen desorption signal was detected by the thermal conductivity detector (TCD) during programmed heating.

2.4. Reaction study

A fixed-bed glass tube microreactor (i.d. 5 mm) was used to test the catalytic activity of the catalyst samples in CO oxidation. Approximately 100 mg of the catalyst powder was packed in the

middle of tubular microreactor between plugs of quartz wool. A thermocouple was inserted into the reactor below the catalyst bed to measure temperature at the catalyst outlet. The tubular reactor was heated from room temperature to the desired temperature in a vertical tubular furnace. The reactant gas mixture of 1% CO, 2% O₂, and the balanced He was introduced at a total flow rate of 100 cm³/min or a gas hourly space velocity (GHSV) ≈ 30,600 h⁻¹. The catalyst was first reduced *in situ* at 200 °C in flowing hydrogen (50 cm³/min) for Ag/TiO₂ for 1 h. After the reduction, the reactant gas mixture was switched into the reactor and maintained at a desired temperature for 20 min. The concentration of CO was monitored by an on-line GC-8ATP (Shimadzu) gas chromatograph equipped with a TCD detector and a Porapak Q column. The conversion of CO was defined as the number of moles of CO converted per the total number of CO in feed stream. The temperature at which conversion reaches 50% (defined as light-off temperature) is used to compare the catalytic activities of the catalyst samples.

3. Results and discussion

3.1. Effect of Si doping on the properties of TiO₂

The XRD patterns of TiO₂ and Si-modified TiO₂ prepared by the solvothermal method are shown in Fig. 1. All the samples exhibited only pure anatase phase TiO₂ without any other phase contamination. The XRD patterns of Si-modified TiO₂ showed the major peak of anatase TiO₂ at 2θ around 25°. Increasing of Si content can affect the broadening of XRD peaks [23]. However, the peak intensity of anatase TiO₂ decreased with increasing Si content, indicating that the crystallite size of TiO₂ became smaller. The crystallite sizes of TiO₂ and Si-modified TiO₂ are shown in Table 1. The crystallite sizes of all Si-modified TiO₂ were smaller than the unmodified TiO₂. The peak position of anatase (1 0 1) and lattice

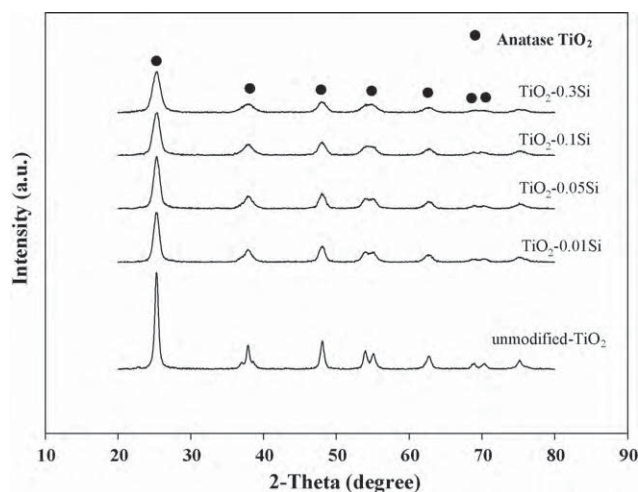


Fig. 1. XRD patterns of Si-modified TiO₂ with different Si/Ti molar ratios.

Table 1

Physical properties and amount of active sites of unmodified TiO₂, Si-modified TiO₂ support and 10%Ag/TiO₂-xSi catalysts.

Sample	Crystallite size (nm)	BET surface area (m ² /g)	Active site of 10%Ag/TiO ₂ -xSi (×10 ²⁰ atom/g-catalyst)
Unmodified TiO ₂	15.0	77	1.27
TiO ₂ -0.01Si	9.8	103	2.10
TiO ₂ -0.05Si	8.5	125	2.02
TiO ₂ -0.1Si	7.0	136	1.98
TiO ₂ -0.3Si	6.4	96	2.46

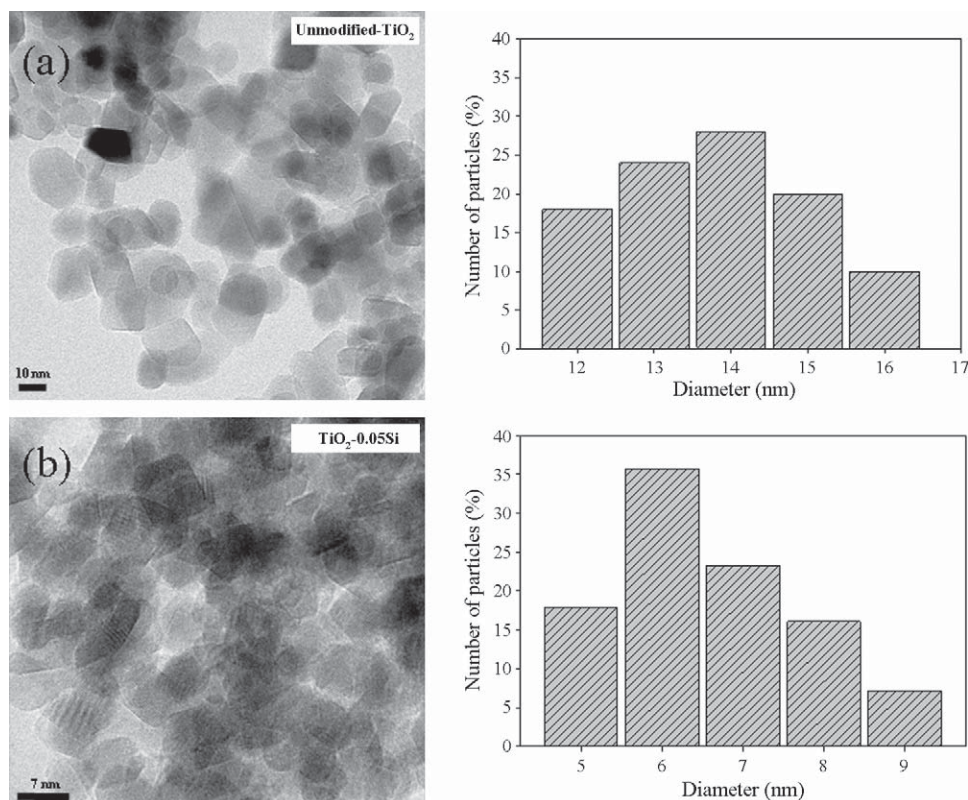


Fig. 2. TEM images and the size distribution of (a) unmodified TiO₂ and (b) TiO₂-0.05Si.

parameters of TiO₂ and Si-modified TiO₂ support are given in Table 2. The anatase (1 0 1) diffraction peaks for all the Si-modified TiO₂ were shifted slightly to a higher angle compared to that of the TiO₂ support, indicating a decrease of the distance between crystal planes which related to the lattice parameters [24]. The decrease of the lattice parameters for the Si-modified TiO₂ compared to the TiO₂ was attributed to an insertion of the smaller ionic radius of Si (0.042 nm) into the lattice of TiO₂ (ionic radius 0.064 nm) [25]. Moreover, the peak intensity of anatase TiO₂ decreased with increasing Si content, indicating that the crystallite size of TiO₂ became smaller.

Fig. 2 shows the TEM images of TiO₂ and TiO₂-0.05Si. The particle size distributions were in the range of 12–16 nm and 5–9 nm for the TiO₂ and the TiO₂-0.05Si, respectively. Such results were in good agreement the XRD results in which the crystallite size of TiO₂ supports decreased with Si doping. The existence of Si in the TiO₂ framework may inhibit the TiO₂ moiety to form large crystal [26]. Moreover, the replacement of Ti by Si atom in TiO₂ lattice can also produce Ti–O–Si bond and the lattice shrinkage because the bond length of Si–O bond (1.59 Å) is shorter than that of Ti–O (1.79 Å) [27], as a consequence the crystallite size of TiO₂ is decreased. As also shown in Table 1, BET surface area of the TiO₂

supports increased with increasing Si content and reached a maximum value of 136 m²/g for the TiO₂-0.1Si. Further increase of Si/Ti to 0.3 resulted in the decrease of BET surface area. Similar results were observed by Jin et al. that the BET surface area of silica-doped TiO₂ prepared by hydrothermal process decreased when the molar ratio of Si/Ti was higher than 0.05 [28].

Fig. 3 shows the FT-IR spectra of Si-modified TiO₂ with the Si/Ti molar ratio between 0.01 and 0.3 in the wave number ranging from 400 to 4000 cm⁻¹. The spectra bands at ca. 1630 and 3400 cm⁻¹ were attributed to H–OH bonds of adsorbed water molecules and hydroxyl group of Ti–OH bonds, respectively [29–31]. The hydroxyl group at 3400 cm⁻¹ of all Si-modified TiO₂ seems to increase compared with the TiO₂ support. These results are in agreement with Chen et al. [32], who reported that the hydroxyl

Table 2

The peak position of anatase and lattice parameters of unmodified TiO₂ and Si-modified TiO₂ support.

Sample	Peak position of anatase (1 0 1)	Lattice parameters (Å)	
	(2θ) (degree)	a (=b)	c
Unmodified TiO ₂	25.28	3.7934	9.5003
TiO ₂ -0.01Si	25.52	3.7528	9.5003
TiO ₂ -0.05Si	25.32	3.7896	9.4523
TiO ₂ -0.1Si	25.40	3.7766	9.4427
TiO ₂ -0.3Si	25.40	3.7766	9.4427

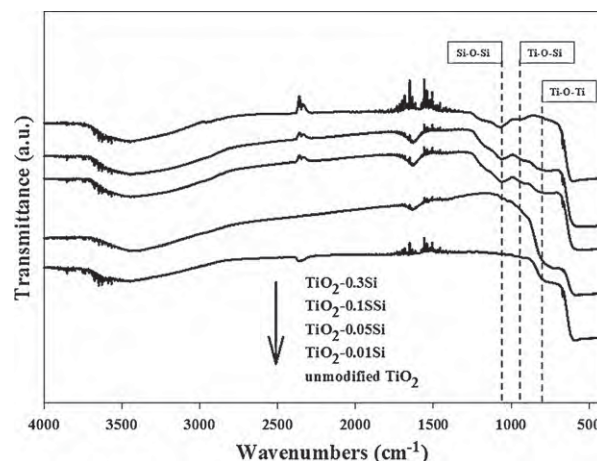


Fig. 3. FT-IR spectra of Si-modified TiO₂ with different Si/Ti molar ratios.

groups of TiO_2 increased after Si doping in non-humidity system. The IR spectra at ca. 700 and 800 cm^{-1} were attributed to Ti–O–Ti bonds in the TiO_2 lattice [33]. It is noticed that the spectra band in the $400\text{--}850\text{ cm}^{-1}$ region became weaker with the increase of Si content, suggesting that the formation of Ti–O–Ti structure was suppressed due to the formation of Ti–O–Si and/or Si–O–Si structure. The presence of Ti–O–Si bond was confirmed by the IR spectra band at ca. 950 cm^{-1} [34–36]. The intensity of Si–O–Si bonds at ca. 1070 cm^{-1} also increased with increasing the Si content. The presence of the amorphous silica could prevent the agglomeration of TiO_2 nanoparticles, leading to a decrease of TiO_2 particle size [37,38]. The metal active sites of Ag/ TiO_2 catalysts were determined by pulse chemisorption and are given in Table 1. It is clearly shown that higher metal dispersion was obtained on the Si-modified TiO_2 . The amount of metal active sites on the Si-modified TiO_2 supported catalysts were nearly two times higher than those supported on the unmodified ones. However, the amount of metal active sites on the Si-modified TiO_2 was quite similar especially for those with the Si/Ti ratio 0.01–0.1.

3.2. Effect of Si doping on the activity of CO oxidation

The CO conversions as a function of reaction temperature for 10%Ag/ TiO_2 with different Si contents in the TiO_2 are shown in Fig. 4. Addition of trace amount of Si in the TiO_2 supports can improve the CO oxidation activity of the TiO_2 supported Ag catalysts. However, there existed an appropriate amount of Si/Ti molar ratio that yielded the higher CO oxidation activity at around 0.05–0.1. At their optimum Si/Ti ratios, the Si-modified TiO_2 supported Ag catalysts showed light-off temperature at 68°C , which were much lower than the corresponding unmodified ones. When the Si contents were higher than their optimum values, the Si-modified TiO_2 supported catalysts exhibited lower CO oxidation activity although these catalysts possessed higher amount of metal active sites as measured by pulse chemisorption. Thus, the modification of TiO_2 with Si atoms not only improved the metal dispersion, but also affected the mechanism of CO oxidation.

The reaction mechanism for catalytic CO oxidation is known to compose of two possible mechanisms (1) the CO molecule and oxygen atom from external source are coadsorbed on metal active site to produce CO_2 and (2) the CO molecule is adsorbed on metal catalyst surface to form intermediate complex and then reacted with surface lattice oxygen atom of TiO_2 support to generate CO_2 . The oxygen from external source in gas phase then dissociates into atomic oxygen and is adsorbed on the oxygen vacancies sites of the TiO_2 support. As suggested by Mguig et al. [39], the latter

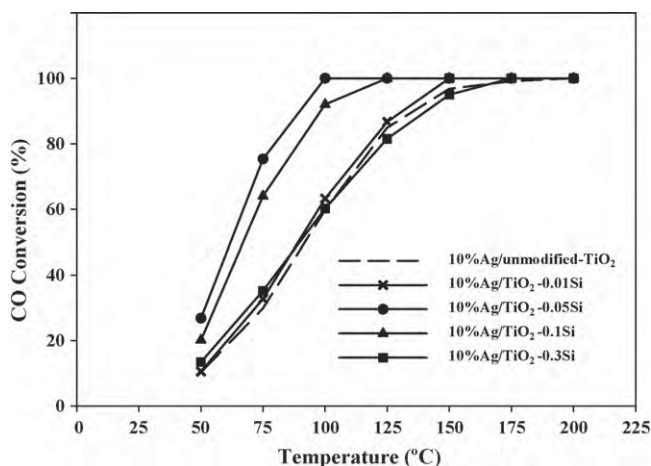


Fig. 4. CO conversion over 10 at.%Ag catalysts supported on Si-modified TiO_2 with different Si/Ti molar ratios.

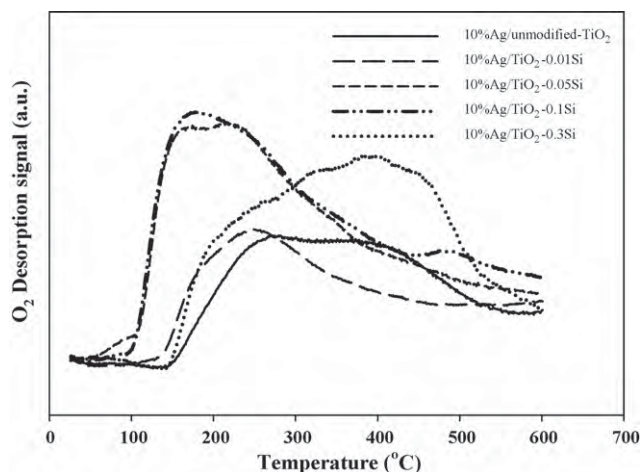


Fig. 5. O_2 -TPD patterns of 10 at.%Ag catalysts supported on Si-modified TiO_2 with different Si/Ti molar ratios.

mechanism occurs more easily on defective surface or basic site surface of metal oxide support. In the present study, the modification of TiO_2 support with trace amount of Si resulted in an increase of the amounts of hydroxyl group and the formation of basic site surface and improved CO oxidation activities. Thus, it is likely that CO oxidation on the Si-modified TiO_2 supported Ag catalysts occurred via such mechanism.

According to the mechanism proposed by Bollinger and Vannice [40] for CO oxidation over Au/ TiO_2 catalysts, the adsorption of CO and O_2 occurred on two different sites, CO adsorbed on Au and O_2 adsorbed on TiO_2 . Then CO reacted with surface lattice oxygen of TiO_2 to form CO_2 leading to the formation of surface oxygen vacancies. During the CO oxidation, these oxygen vacancies were filled by chemisorbed oxygen species from gas phase. The oxygen adsorption and desorption behaviors of the Ag/ TiO_2 catalysts were investigated by using O_2 -TPD experiments and the results are shown in Fig. 5. The Si-modified TiO_2 supported Ag catalysts with optimum Si/Ti ratios exhibited much lower desorption temperature and larger amount of desorbed O_2 compared to the non-modified ones and the ones with excess Si. According to Iwamoto et al. [41], there are three kinds of adsorbed oxygen species on TiO_2 surface. The adsorbed oxygen consists of weakly adsorbed surface oxygen, strongly adsorbed surface oxygen and surface lattice oxygen. The weakly adsorbed oxygen desorption in the range of $100\text{--}180^\circ\text{C}$ and $\sim 230^\circ\text{C}$ were assigned to O_2^- and O^- species, respectively [42]. The desorption temperature of strongly adsorbed surface oxygen and surface lattice oxygen were reported in the range of $470\text{--}490^\circ\text{C}$ and $810\text{--}870^\circ\text{C}$, respectively [43,44]. The results demonstrated that the Si-modified TiO_2 supported Ag catalysts with optimum Si/Ti ratios produced the highest amount of O_2^- and O^- species whereas the non-modified ones and the ones with excess Si produced O^- species and strongly adsorbed surface oxygen. It has been reported that the adsorbed O^- species were the most active species for CO oxidation [8]. In addition, Qu et al. [45] suggested that the strongly adsorbed surface oxygen species blocks the adsorption and diffusion of weakly adsorbed surface oxygen, causing a decrease in the CO oxidation activity of the catalysts.

The results in this work show that oxygen in Ag/ $\text{TiO}_2\text{--}0.05\text{Si}$ and Ag/ $\text{TiO}_2\text{--}0.1\text{Si}$ catalysts desorbed more easily so that the catalysts exhibited higher CO oxidation activity. It is suggested that the formation of Ti–O–Si bonds produced an appreciable change in the electronic properties of these catalysts. Generally, TiO_2 was classified as a support which exhibits the strong metal-support interaction with precious metals. Bernal et al. [46] reported that the temperatures of oxygen desorption from metal catalyst surface

increased when a strong interaction between the metal particles and support occurred. The addition of Si into TiO₂ lattice to form Ti–O–Si bonds may lead to a decrease of the metal-support interaction and resulted in a decrease of oxygen desorption temperature. In other words, the adsorbed oxygen on the Si-modified TiO₂ with optimum Si/Ti ratios can be dissociated to atomic species which desorbed at lower temperature. Moreover, the presence of Si in TiO₂ could decrease the strength of surface lattice oxygen bonding, resulted in higher mobility of lattice oxygen which has been reported to be beneficial for CO oxidation [47,44].

On the other hand, an excess Si content in the TiO₂ support (i.e., for Si/Ti = 0.3) exhibited the increase of amorphous SiO₂ formation which revealed by Si–O–Si bonds from FT-IR results. Qu et al. [48] reported that interaction between Ag and SiO₂ became strongly when the catalyst was pretreated in oxygen at high temperature like a calcination of the catalyst in an oxygen atmosphere. Thus, the formation of SiO₂ in TiO₂ lattice led to a shift of oxygen desorption temperature towards higher temperature and decreased the catalytic activity in CO oxidation.

4. Conclusions

The presence of trace amount of Si atoms in the TiO₂ supports with Si/Ti = 0.05–0.1 has resulted in an improved catalytic performance of Ag/TiO₂ catalysts in the CO oxidation. The insertion of Si atoms into the TiO₂ lattice in the form of Ti–O–Si not only increased the metal active sites by increasing specific surface area of the catalyst and inhibition the agglomeration of TiO₂ crystallites but also altered the strength of O₂ adsorption–desorption behavior on the catalyst surface. As shown by the O₂-TPD results, the Si-modified TiO₂ supported catalysts exhibited higher amount of oxygen adsorption and lower desorption temperature, which could promote the formation of active oxygen species and increase the mobility of lattice oxygen so that the catalytic activity was enhanced. An excess Si content (i.e., Si/Ti = 0.3), on the other hand, resulted in higher oxygen desorption temperature and no improvement of the catalyst activity, due probably to the formation of amorphous SiO₂.

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Thermodynamic analysis of calcium oxide assisted hydrogen production from biogas

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ABSTRACT

This paper investigates calcium oxide assisted hydrogen production from biogas. Preliminary experiments were performed to compare the catalytic performance of combined carbon dioxide reforming and partial oxidation of biogas among four different adsorbent (CaO)/catalyst (Ni/SiO₂-MgO) arrangements; i.e. (i) Ni/SiO₂-MgO before CaO, (ii) CaO before Ni/SiO₂-MgO, (iii) Ni/SiO₂-MgO mixed with CaO, and (iv) Ni/SiO₂-MgO without CaO. The mixture of CaO and Ni/SiO₂-MgO was found to be the best arrangement, offering the highest hydrogen yield. Thermodynamic investigation of the integrated sorption-reaction systems for hydrogen production from biogas was performed. The system can be operated under thermal neutral condition when appropriate operating parameters are adjusted. Finally based on the thermal neutral operation, the effects of H₂O/CH₄ and CaO/CH₄ ratios on the required O₂/CH₄ ratio, hydrogen yield, hydrogen concentration and CO/H₂ ratio in product were determined. Obviously the use of CaO adsorbent can improve hydrogen production and there is an optimum H₂O/CH₄ ratio which offers the highest hydrogen production at each CaO/CH₄ ratio. Increasing H₂O/CH₄ ratio generally increases H₂/CO ratio but decreases hydrogen concentration in the product.

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1. Introduction

Energy production from renewable sources is one of several approaches to reduce emissions of greenhouse gases (GHG). Nowadays, GHG is one of significant problems that have a great impact on global warming. About 75% of the anthropogenic carbon dioxide (CO₂) emissions to the atmosphere during the past 20 years are due to fossil fuel burning [1,2]. In addition to CO₂, methane (CH₄) produced in natural environments from anaerobic degradation of organic substrates is another major constituent significantly contributing to a greenhouse effect with a 23-fold higher global warming potential than CO₂ [3,4]. With the increasing concern on environmental problems, many countries are pursuing efforts to develop renewable energy sources and fuels with lower carbon content as an alternative future energy resource. Increasing fuel combustion efficiency and capturing/storing CO₂ produced are also important aspects in developing new energy technologies.

Hydrogen is considered to be the most promising future energy carrier [2,5]. A hydrogen-based energy economy coupled with the anticipated limits on CO₂ emissions provides a good opportunity for the investigation of H₂ production processes that are more energy-efficient and environmental friendly. A sorption-enhanced H₂ production (SEHP) in which the hydrocarbon reforming, water-gas shift, and CO₂ removal reactions occur simultaneously at high temperatures over a mixture of reforming catalyst and CO₂ sorbent, could be a potential alternative. In the SEHP process, CO₂ is reacted with a solid sorbent (adsorption/carbonation step) and converted to a solid carbonate. Regenerating the sorbent (desorption/calcination step) results in releasing CO₂ which is in a form suitable for storage. Several sorbent materials, i.e. calcium oxide [6], lithium oxides [6–9], hydrotalcites [6,10,11], double salts [6,12], and basic alumina [6,13], have been studied for the sorption of CO₂ at high temperatures. Recently, calcium oxide (CaO) has been examined thoroughly as a suitable sorbent for SEHP processes [6,14–20]. It was reported to be thermodynamically the best candidate among various metal oxides for CO₂ capture in zero emission power generation systems [2,20]. In addition, CaO is cheap and readily available in nature. Thus, the CaO sorption process has been a well-known CO₂ capture technology nowadays.

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This study concentrates on the production of H_2 from biogas via a sorption-enhanced system. The experiment of the combined carbon dioxide reforming and partial oxidation of biogas over an industrial Ni/SiO₂-MgO catalyst and a CaO adsorbent was carried out to investigate the effect of an adsorbent and catalyst bed arrangement on the reaction performance. Further, a thermodynamic analysis was performed to investigate the effects of temperature, oxygen, water, and CaO sorbent under a thermal neutral operation in which no external heat is required to sustain the reactor operation.

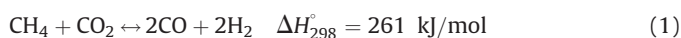
2. Theory

2.1. Sorption-enhanced dry reforming and partial oxidation of biogas

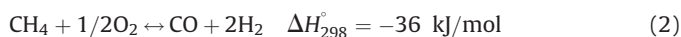
2.1.1. Reforming and partial oxidation

The main reactions taking place in the system are:

Methane dry reforming with carbon dioxide:

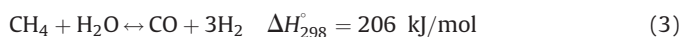


Methane partial oxidation with oxygen:

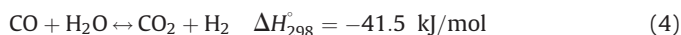


When steam is introduced to the reaction system, the steam reforming of methane and the water gas shift reaction can be occurred as follows.

Methane steam reforming reaction:



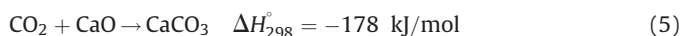
Water gas shift reaction:



Methane reforming with carbon dioxide (Eq. (1)) and steam (Eq. (3)) are highly endothermic, the forward reaction are thermodynamically favored with high operating temperature and low pressure while methane partial oxidation (Eq. (2)) and water gas shift reaction (Eq. (4)) are mildly exothermic.

2.1.2. Sorption of carbon dioxide on calcium oxide

Carbon dioxide sorption (carbonation reaction) on calcium oxide can be explained by the following reaction:



Utilization of CaO to capture carbon dioxide can improve the operation performance as the exothermic heat from carbon dioxide sorption can be utilized for the endothermic reactions.

2.2. Thermodynamic analysis

For understanding the advantages of combining sorption and reaction for H_2 production and studying of suitable operating condition, a thermodynamic analysis of the important reactions (Eqs. (1)–(5)) were investigated. Aspen Plus simulator was used for equilibrium calculations. The minimization of Gibbs free energy method has been used for predicting the product compositions at equilibrium. The products are in both gas phase i.e. CH_4 , CO , CO_2 , O_2 , H_2 , H_2O and solid phase i.e. C . The effect of operating parameters, i.e. H_2O/CH_4 and CaO/CH_4 ratios were investigated. The material and energy balances were solved in order to determine the thermal neutral operation in which no external heat is required to sustain the reactor operation.

3. Experimental

A commercial-grade reforming catalyst, Ni/SiO₂-MgO, containing 55 wt.% of nickel supplied from Japan and a commercial-grade calcium oxide adsorbent supplied from Riedel-de Haën were employed in this study. The catalyst was cylindrical extrudate with a diameter of 3 mm and a length of 3 mm. Silicon carbide supplied from Fluka with an average size of 40–100 mesh was used as a dilution material for the catalyst. The reaction was carried out in a reaction system described in our previous work [21]. The reactor was a quartz tube (internal diameter = 0.011 m, length = 0.5 m) heated by a temperature-controlled electric oven. Experiments were performed using Ni/SiO₂-MgO catalyst (0.1314 g) diluted with silicon carbide (0.438 g) and CaO adsorbent (0.657 g). CaO adsorbent acts as a CO₂ acceptor in the sorption-enhanced system. As shown in Fig. 1, four different bed arrangements in the sorption-enhanced operation were considered as follows: (i) Ni/SiO₂-MgO before CaO, (ii) CaO before Ni/SiO₂-MgO, (iii) Ni/SiO₂-MgO mixed with CaO, and (iv) Ni/SiO₂-MgO without adsorbent. High pure CH_4 (99.999%), CO_2 (99.999%) and O_2 (99.99%) were used as the reactant gases. Argon was used for purging the system. The reaction was taken place at 1023 K and atmospheric pressure. The catalyst was reduced in a hydrogen flow (30 cm³/min) for 1 h and then the gas feed containing CH_4 (12.5 cm³/min), CO_2 (12.5 cm³/min) and O_2 (6.25 cm³/min) was switched to the reactor. It should be noted that with the difference in bed arrangements it becomes difficult to keep the same space velocity and contact time for each configuration. Therefore, the comparison of reaction performance among the different arrangements was based on the

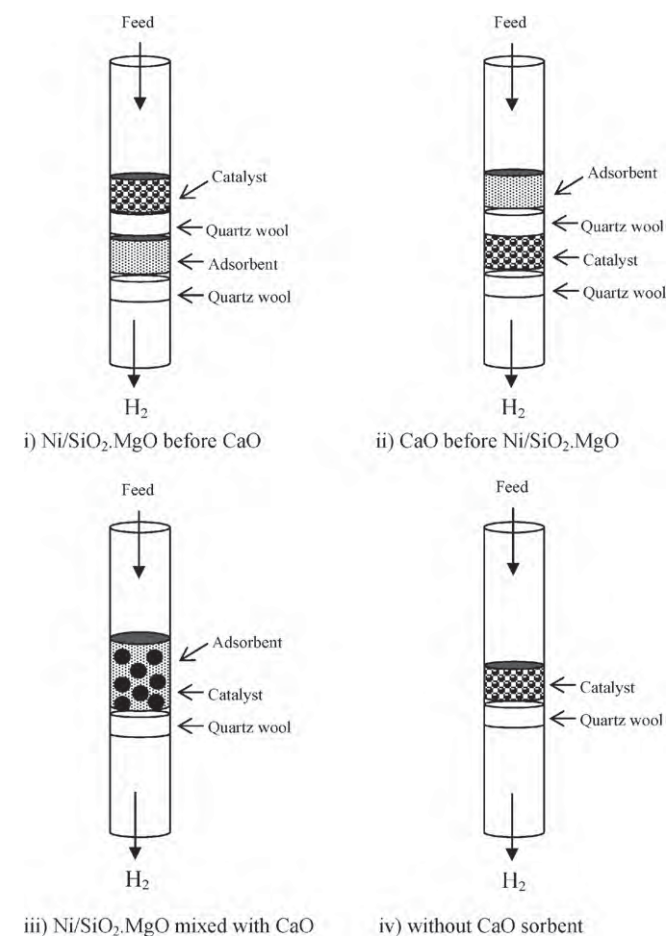


Fig. 1. Different adsorbent/catalyst arrangements in the sorption-enhanced operation.

same ratio of gas feed rate per catalyst weight. The composition of exit gas effluent was analyzed every 10 min by a TCD gas chromatograph (Shimadzu GC-8A, Japan) equipped with a Porapak-Q and Molecular Sieve 5A column. The H_2 yield were defined as

$$H_2 \text{ yield} = \frac{H_2 \text{ molar flow rate}/2}{CH_4 \text{ molar feed flow rate}} \quad (6)$$

4. Results and discussion

A preliminary set of experiments was performed to determine a suitable adsorbent/catalyst arrangement for hydrogen production from simulated biogas, a mixture of CH_4 (50 mol%) and CO_2 (50 mol%). Hydrogen yields achieved from the operation under four different bed arrangements are shown in Fig. 2. It can be seen that for the case without CaO (conventional operation), hydrogen yield initially increases and levels off at a hydrogen yield of about 57%. For the case of packing $Ni/SiO_2 \cdot MgO$ before CaO, it shows similar behavior as the first case in term of hydrogen yield, indicating that the presence of CaO after the catalyst bed does not help improving the reactions in the system. However, it was observed that hydrogen concentration in the exit gas is considerably higher than the first case since CO_2 in the reaction product was adsorbed by CaO. Importantly, the improvement in hydrogen yield was observed for the cases of packing CaO before $Ni/SiO_2 \cdot MgO$ and $Ni/SiO_2 \cdot MgO$ mixed with CaO with. For the case of packing CaO before the catalyst, in which some CO_2 in the feed was removed before reaching the subsequent catalyst bed, the increasing of hydrogen yield was observed over 20 min of reaction time. As for the case of mixing CaO with the catalyst in the bed, the improvement of hydrogen yield becomes more significant and the superior yield is observed until 80 min of reaction time. Previous report suggested that with pure CO_2 of 1 atm, the minimum temperature for CO_2 desorption from $CaCO_3$ is 1173 K [22]. Hence, CaO could be assumed effective for CO_2 adsorption in the range of operating temperature in our study. However, it should be noted that for all experiments, hydrogen yields always approached the same value of about 57% after prolonged period since the sorption of CO_2 by CaO become insignificant when most of CaO is converted to $CaCO_3$. In addition, the study further demonstrated that when sorbent bed is appropriately integrated in the reaction system, the values of hydrogen yield higher than the equilibrium value (75%) can be achieved.

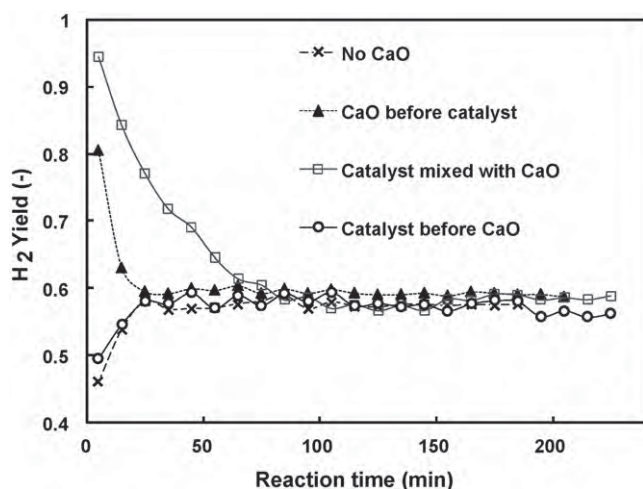


Fig. 2. Hydrogen yield achieved from different adsorbent/catalyst arrangements ($T = 1023$ K, $CH_4:CO_2:O_2 = 1:1:0.5$).

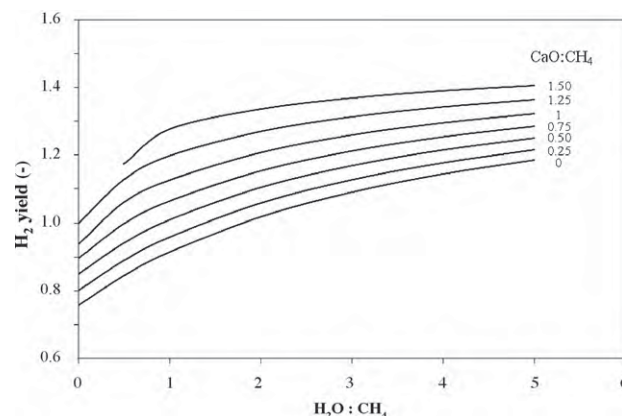


Fig. 3. Hydrogen yield in the CaO assisted hydrogen production system ($T = 1073$ K and $O_2:CH_4 = 0.5$).

According to these preliminary results, it is obvious that the use of CaO in the combined carbon dioxide reforming and partial oxidation of biogas particularly under the mode of mixture of CaO and $Ni/SiO_2 \cdot MgO$ can improve the hydrogen yield compared to the conventional system without CaO. Therefore, the reaction system under the mode of mixture of CaO and $Ni/SiO_2 \cdot MgO$ was selected for further studies. It is noted that for practical application of this adsorbent/catalyst system under steady-state condition, a fluidized bed reactor with continuous feeds of a gas mixture and CaO is generally considered as a suitable option for the sorption-enhanced hydrogen production from biogas. When this reactor is equipped with a regenerator for regenerating $CaCO_3$ to CaO, the system can be operated continuously under steady-state condition. In addition, the removed CO_2 can be further sequestered, if necessary, in order to reduce the amount of CO_2 released to the environment.

As the next step, the technical feasibility of the above system without a regenerator was studied based on thermodynamic analysis. The reactions taking place are assumed at equilibrium compositions and the feed biogas is assumed to consist of 50% CH_4 and 50% CO_2 . The effects of some major operating parameters; i.e. H_2O/CH_4 , and CaO/CH_4 ratios on hydrogen yield, hydrogen concentration, CO/H_2 ratio in product gas, and overall enthalpy change were investigated in order to understand the role and behavior of CaO assisted hydrogen production from biogas. It is noted that the inlet O_2/CH_4 ratio and operating temperature was fixed at 0.5 and 1073 K, respectively.

Figs. 3 and 4 show the hydrogen yield and enthalpy change of the system at various values of H_2O/CH_4 and CaO/CH_4 ratios. It was

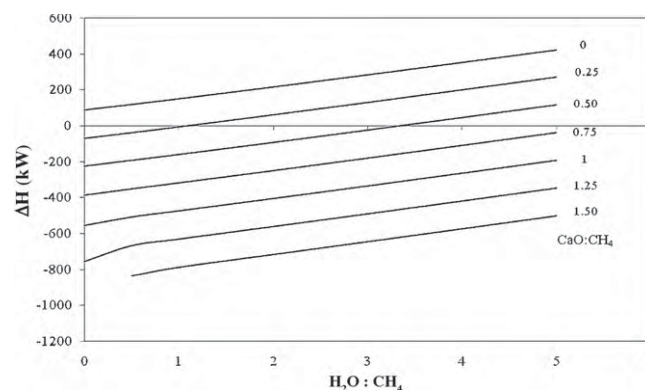


Fig. 4. Overall enthalpy change in the CaO assisted hydrogen production system ($T = 1073$ K and $O_2:CH_4 = 0.5$).

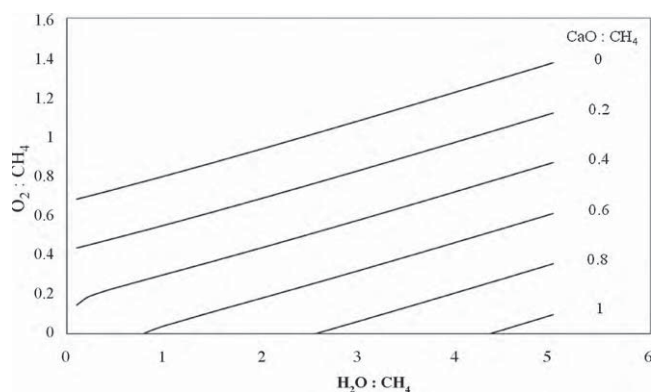


Fig. 5. O_2/CH_4 ratio required for thermal neutral operation of the CaO assisted hydrogen production system ($T = 1073$ K).

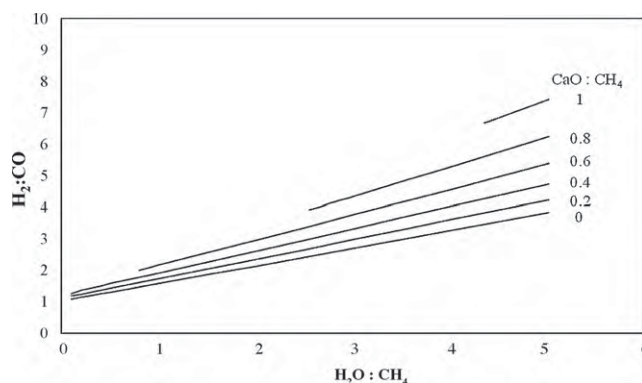


Fig. 7. H_2/CO ratio at the thermal neutral operation of the CaO assisted hydrogen production system ($T = 1073$ K).

demonstrated that at low H_2O/CH_4 ratio and without the presence of CaO, hydrogen yield as low as 37.5% is achieved because the hydrogen production is predominately governed by the carbon dioxide reforming and partial oxidation which offer low hydrogen. When water is added in the reaction system, more hydrogen is observed according to the promotion of methane steam reforming and water gas shift reaction. The highly endothermic steam reforming causes the enthalpy change to become less negative (Fig. 4). Under the presence of CaO in the system, the removal of carbon dioxide can further increase the hydrogen yield by shifting the water gas shift reaction and consequently shifting the methane steam reforming. The enthalpy change becomes more negative as the carbonation (Eq. (5)) is a highly exothermic reaction. From Fig. 4, it is evident that when the operating parameters are carefully adjusted, the system can be operated at a thermal neutral condition ($\Delta H = 0$) in which the heat generated is equal to the heat consumed. For example, at $O_2/CH_4 = 0.5$, the suitable values of H_2O/CH_4 ratio are 1.1 and 3.3 when the CaO/CH_4 ratios are 0.25 and 0.5, respectively.

In the following studies, only the results at thermal neutral condition are determined as it is a desirable condition for practical operations – no effort on heat addition to or heat removal from the system is required. The values of O_2/CH_4 ratio required at different H_2O/CH_4 and CaO/CH_4 ratios are shown in Fig. 5. It is obvious that higher O_2/CH_4 ratios are required when the system is operated at higher H_2O/CH_4 ratios while lower O_2/CH_4 ratios are needed at higher CaO/CH_4 ratios. This is because of the endothermic and exothermic natures of the steam reforming and carbonation reactions, respectively. Figs. 6–8 show the corresponding hydrogen yield, H_2/CO ratio and hydrogen concentration in product,

respectively. Unlike the results shown in Fig. 2 (isothermal condition), there is an optimum H_2O/CH_4 ratio which provides the highest hydrogen yield for each CaO/CH_4 ratio in the thermal neutral operation (Fig. 6). At low H_2O/CH_4 ratio, low hydrogen yield is obtained as most hydrogen is derived from the carbon dioxide reforming and the partial oxidation of methane which give lower hydrogen than does the steam reforming. When operating at a higher H_2O/CH_4 ratio, higher hydrogen yield is achieved from the promotion of methane steam reforming and water gas shift reaction as evident by the observed higher H_2/CO ratio in the product (Fig. 7). However, when the system is operated at too high values of H_2O/CH_4 , operation at higher O_2/CH_4 ratios is required as shown in Fig. 5 so that the exothermic heat generated from the partial oxidation and complete combustion of methane is sufficient for providing the increased endothermic heat demand from the presence of higher extent of steam. Therefore, less hydrogen is generated. From Fig. 8, it is observed that the addition of extra steam lowers the hydrogen concentration in most cases due to the dilution of gas product by excess water and the requirement of higher oxygen in the system.

When the reactions are incorporated with the addition of CaO, it is evident that the CaO assisted hydrogen production shows beneficial effects on all the hydrogen yield, H_2/CO ratio and hydrogen concentration. The removal of CO_2 from the reaction system by CaO sorption promotes the water gas shift reaction and subsequently the steam reforming, and therefore, increases all the hydrogen yield, hydrogen concentration and H_2/CO ratio. In addition, the exothermic heat generated from the carbonation reduces the requirement of O_2/CH_4 ratio and thus suppresses the hydrogen production from the partial oxidation

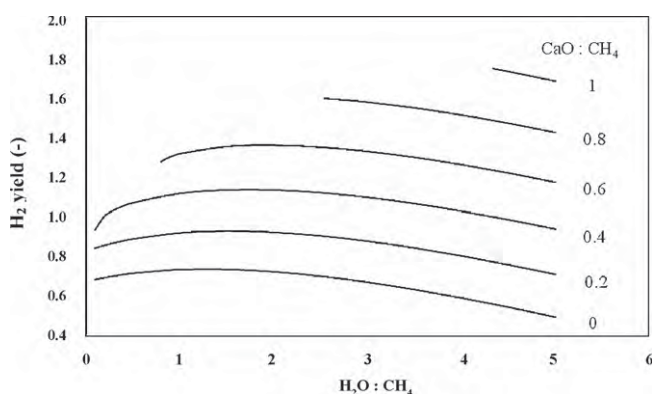


Fig. 6. Hydrogen yield at the thermal neutral operation of the CaO assisted hydrogen production system ($T = 1073$ K).

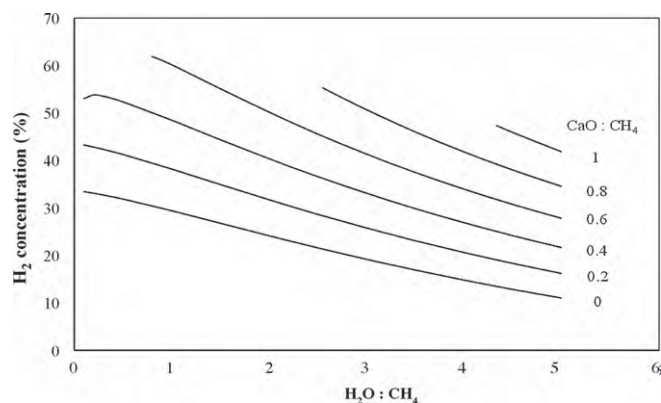


Fig. 8. Hydrogen concentration at the thermal neutral operation of the CaO assisted hydrogen production system ($T = 1073$ K).

reaction which offers lower hydrogen production and hydrogen concentration.

5. Conclusion

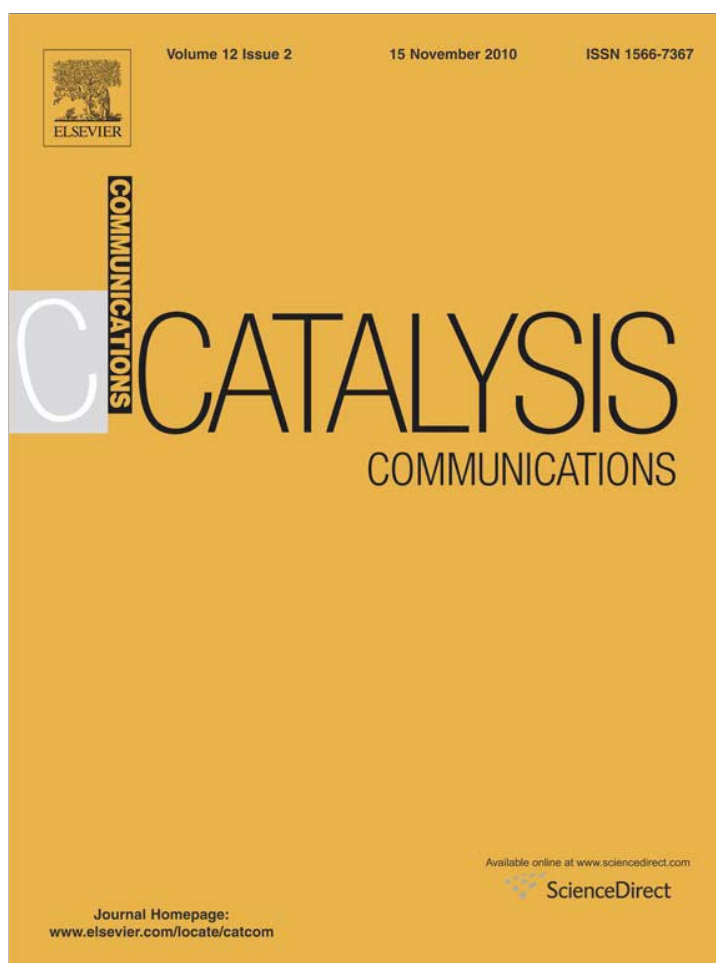
The reaction tests for hydrogen production from biogas using four different adsorbent/catalyst arrangements; (i) Ni/SiO₂-MgO before CaO, (ii) CaO before Ni/SiO₂-MgO, (iii) Ni/SiO₂-MgO mixed with CaO, and (iv) Ni/SiO₂-MgO without CaO, indicated that the CaO assisted hydrogen production is best to be performed under an operation with mixture of CaO and Ni/SiO₂-MgO. The thermodynamic investigation revealed that the H₂O/CH₄, CaO/CH₄ and O₂/CH₄ ratios can be appropriately adjusted to achieve thermal neutral condition in which the system requires no external heat source for the operation. Based on this condition, at a higher H₂O/CH₄ feed ratio, the system requires either higher O₂/CH₄ or CaO/CH₄ ratio to maintain the thermal neutral operation. It is clearly demonstrated that the use of CaO adsorbent can promote the hydrogen production and hydrogen concentration in the product. In addition, there is an optimum H₂O/CH₄ ratio which offers the highest hydrogen production at each CaO/CH₄ ratio.

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Catalysis Communications

journal homepage: www.elsevier.com/locate/catcomElucidation of the basicity dependence of 1-butene isomerization on MgO/Mg(OH)₂ catalystsJiraporn Puriwat^a, Wasu Chaitree^a, Kongkiat Suriye^b, Siraprapa Dokjampa^b,
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ABSTRACT

The gas-phase isomerization of 1-butene to 2-butene was investigated on the MgO/Mg(OH)₂ catalysts containing different basicities (i.e., weak, medium, and strong basic sites). The isomerization reaction mainly proceeded on either the strong or the medium strength basic sites while the weak basic sites had little impact on the isomerization activity. As revealed by CO₂-temperature program desorption (CO₂-TPD), Fourier-transformed-infrared spectroscopy (FT-IR), and electron spin resonance (ESR), the crystalline MgO contained both weak and strong basic sites while the Mg(OH)₂ phase exhibited only the medium strength one. The strong basic sites of MgO were correlated well with the presence of oxygen atoms in the lattice of crystalline MgO. The medium strength basic sites in Mg(OH)₂, on the other hand, were arisen from the hydroxyl groups in the Mg(OH)₂ structure.

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1. Introduction

In the field of heterogeneous catalysis, many reactions involve acidic–basic properties of the catalyst surface. Compared to the wide use of heterogeneous acid catalysts, commercialization of heterogeneous base catalysts and characterization of solid bases have been less reported [1,2]. According to a survey by Tanabe and Holderich [2], the number of industrial processes that use solid acids, solid bases, and acid–base bifunctional catalysts are 103, 10, and 14, respectively. Basic catalysts are active and selective for various reactions including isomerization, dehydrogenation, amination, hydrogenation, alkylation, and condensation [3]. Many of these reactions have been carried out industrially using liquid base catalysts. The replacement of liquid bases by solid base catalysts would have the advantage such as decreasing corrosion and environmental problems and easier separation and recovery of the catalysts [4]. The fundamental study on the structure, reactivity, and deactivation of solid bases are, therefore, necessary before they can be widely used as the solid acid catalysts [5].

Magnesium oxide (MgO) is one of the well-known basic catalysts. It is interesting in its essential basic surface character, which makes an effective catalyst and catalyst support [6]. Besides O^{2−} sites, hydroxyl groups also act as basic sites and have been shown to promote basic

reactions [7]. In addition, it has the ability to stabilize metals in unusual oxidation states and to retard sintering and evaporation of the metal atoms [8,9].

Due to the rising demand of propylene, the isomerization of 1-butene to 2-butene on MgO catalysts has now become an important reaction in the metathesis of ethylene and 2-butene for propylene production [10,11]. However, little is known about the active sites of the MgO basic catalyst in 1-butene isomerization reaction and controversy still exists. For examples, Baird and Lunsford [12] suggested that electron donors, presumably the strongly basic O^{2−} ions located on the corners of the cubic oxide lattice are related to the active site for the isomerization of 1-butene. Matsuda et al. [13,14] reported that the isomerization activity could be correlated with stronger basicity than H⁺ = 22.3 and was inactive on MgO catalysts existing only in the weak basic sites. In addition, Klabunde and Matsushashi [15] concluded that surface defects are responsible for 1-butene isomerization.

The purpose of this study was to elucidate the dependence of basicity of the isomerization of 1-butene on MgO and Mg(OH)₂ catalysts. The catalysts were prepared by co-precipitation method using Mg(NO₃)₂ and KOH. The basic properties of the catalysts were varied by changing the calcination temperature. The catalyst activities were evaluated in the gas-phase isomerization of 1-butene to 2-butene. Various analytic techniques have been employed in order to determine the physical and basic properties of the catalysts including X-ray diffraction (XRD), N₂ physisorption, CO₂-TPD, Fourier-transformed-infrared spectroscopy (FT-IR), and electron spin resonance (ESR).

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2. Experimental

2.1. Catalyst preparation

The catalysts were synthesized by co-precipitation method using magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Sigma Aldrich) and potassium hydroxide (KOH) (AnalaR) as the starting materials. Firstly, 0.8 M of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.9 M of KOH solutions were prepared in de-ionized water. These two solutions were added dropwise into 200 cm^3 of de-ionized water under vigorous stirring. The pH was controlled at 11–12. Then, the complete solution was first separated by centrifuging and the solid product washed 5 times in de-ionized water. The white paste was subsequently dried in ambient air overnight and in an oven at 80 °C for 24 h. Finally, the white solid was calcined at various temperatures of 200, 400, 600 and 800 °C for 2 h in air with a ramp rate of 4 °C/min. After thermal treatment, the synthesized catalysts were immediately kept in vials and then preserved in a desiccator to prevent from surface hydration. The calcined samples were denoted as MgO200, MgO400, MgO600, and MgO800 according to the calcination temperature used.

2.2. Catalyst characterization

The XRD patterns were collected using a SIEMENS XRD D5000 diffractometer with $\text{Cu K}\alpha$ radiation and a Ni filter in 10–80° 2 θ angular regions. The crystallite size of samples was calculated using the Scherrer's equation. The BET surface area was determined by N_2 physisorption using a Micromeritics ASAP 2000 automated system. Each sample was degassed at 200 °C for 4 h prior to N_2 physisorption. The CO_2 -TPD was performed to determine the basicity of MgO catalysts using a Micromeritic Chemisorb 2750 automated system. Before adsorption, the sample was pretreated in He for 1 h (flow rate 50 cm^3/min) at the temperature which MgO was calcined. Then, it was cooled down to 100 °C and subsequently adsorbed by CO_2 for 1 h. The temperature-programmed desorption was carried out at a constant rate of 10 °C/min from ambient to 750 °C. The ESR was performed in a JEOL model JES-RE2X at room temperature. The hydroxyl groups of the catalysts were identified by FT-IR using a Nicolet 6700TM spectrometer in the range of 3800–3400 cm^{-1} at a resolution of 4.0 cm^{-1} . The catalyst morphology was observed using a Hitachi S-3400N scanning electron microscope. For the pre-adsorbed CO_2 FT-IR experiments, the catalysts were first pretreated *ex-situ* in He flow 50 cm^3/min in a quartz cell at the temperature which they were

calcined. Then, the samples were cooled down to 100 °C and subsequently followed by CO_2 adsorption for 1 h and purging with He for 30 min. The infrared spectra of the pre-adsorbed CO_2 samples were collected using the Nicolet 6700 spectrometer.

2.3. Reaction study

The gas-phase isomerization of 1-butene was carried out in a stainless steel 316 down flow reactor at 300 °C and atmospheric pressure. For a typical run, 10% 1-butene in nitrogen was used as reactant and approximately 0.3 g of catalyst was packed in the reactor. The total flow rate was 26 cm^3/min composed of 2.6 cm^3/min of the reactant and 23.4 cm^3/min of N_2 carrier gas. The composition of products and feed stream were analyzed by a Shimadzu GC-2014 gas chromatograph equipped with FID detector (aluminum oxide porous layer open tubular capillary column).

3. Results and discussion

3.1. Physical properties of the prepared catalysts

The XRD patterns of the prepared catalysts are shown in Fig. 1. For the uncalcined powder and the MgO200 sample, the characteristic diffraction peaks corresponding to $\text{Mg}(\text{OH})_2$ phase were apparent at 2 θ degrees = 18.6°, 32.9°, 38.1°, 50.9°, 58.7°, 62.1°, 68.3° and 72.1° [16–19]. For those calcined at 400 °C and higher temperature, the diffraction peaks corresponding to MgO crystalline can be observed at 2 θ degrees = 37.0°, 43.0°, 62.4°, 74.8° and 78.7° [16,18]. The TGA results (not shown) confirmed that the $\text{Mg}(\text{OH})_2$ was completely transformed into MgO at the temperature ≥ 400 °C.

The physical properties of the uncalcined and calcined MgO at various calcination temperatures are shown in Table 1. The average crystallite sizes of $\text{Mg}(\text{OH})_2$ phase in the uncalcined and the MgO200 samples were determined to be 17.1–17.4 nm with the corresponding BET surface area 42–46 m^2/g . For the sample calcined at 400 °C in which only the MgO crystalline phase was observed, the crystallite size was 6.8 nm. A significant decrease of primary particle size when $\text{Mg}(\text{OH})_2$ was transformed into MgO crystalline phase can be explained by the elimination of water and fragmentation of primary particle [20]. An increase in calcination temperature of MgO from 400 to 800 °C led to an increase of crystallite size from 6.8 to 16.0 nm and as a consequence the BET surface area decreased from 160 to 59 m^2/g , respectively due to sintering of the MgO particles. Moreover, the

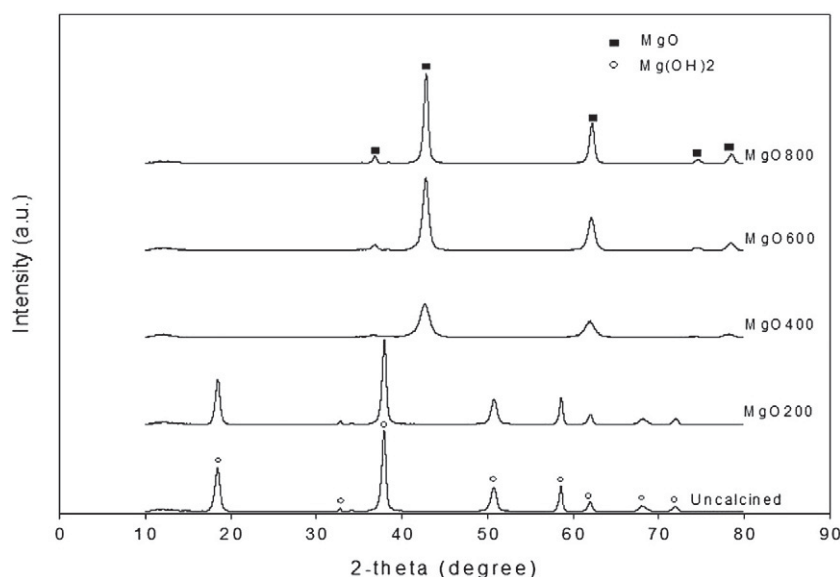


Fig. 1. The XRD patterns of MgO/ $\text{Mg}(\text{OH})_2$ catalysts calcined at various temperatures.

Table 1
The phase transformation and physical properties of MgO/Mg(OH)₂ calcined at various temperatures.

Temperature (°C)	Phase ^a	Crystallite size (nm) ^a	Surface area (m ² /g) ^b	Pore size (nm) ^b
Uncalcined	Mg(OH) ₂	17.4	42	34
200	Mg(OH) ₂	17.1	46	37
400	MgO	6.8	180	3, 43
600	MgO	11.1	91	15
800	MgO	16.0	59	24

^a Based on the XRD results.

^b Based on N₂ physisorption and the BJH method.

bimodal pore structure was observed for the MgO400 sample while the other samples contained only unimodal pore. The SEM micrographs of the various MgO/Mg(OH)₂ catalysts calcined at different temperatures are provided in Fig. 2. There was no difference in particle size/shape of the catalysts in which a flower-like shape was observed.

3.2. Identification of the basicity by FT-IR, CO₂-TPD, and ESR

The hydroxyl groups in the prepared catalysts were determined from FT-IR analysis. Fig. 3(a) shows intense narrow peaks around 3700 cm⁻¹, indicating the presence of hydroxyl groups in the Mg(OH)₂ phase [19,21–23] while Fig. 3(b) shows broad band peaks in the range of 3400–3750 cm⁻¹, which were attributed to the isolated hydroxyl groups on the MgO samples [24,25].

The TPD profiles of CO₂ desorbed in the temperature range of 100–750 °C are shown in Fig. 4. The CO₂ desorption profiles consisted of three major peaks corresponding to different interactions of CO₂ with MgO surface sites. The desorption peaks in the range of 100–300 °C, 300–550 °C, and 550–750 °C were categorized into the weak, the medium, and the strong basic sites, respectively. The amounts of CO₂ desorption in each temperature range were calculated based on the area under the desorption peaks and are given Table 2. For the uncalcined sample and the MgO200, only the medium strength basic sites were presented. The uncalcined sample showed a higher amount of medium basic sites compared to the MgO200.

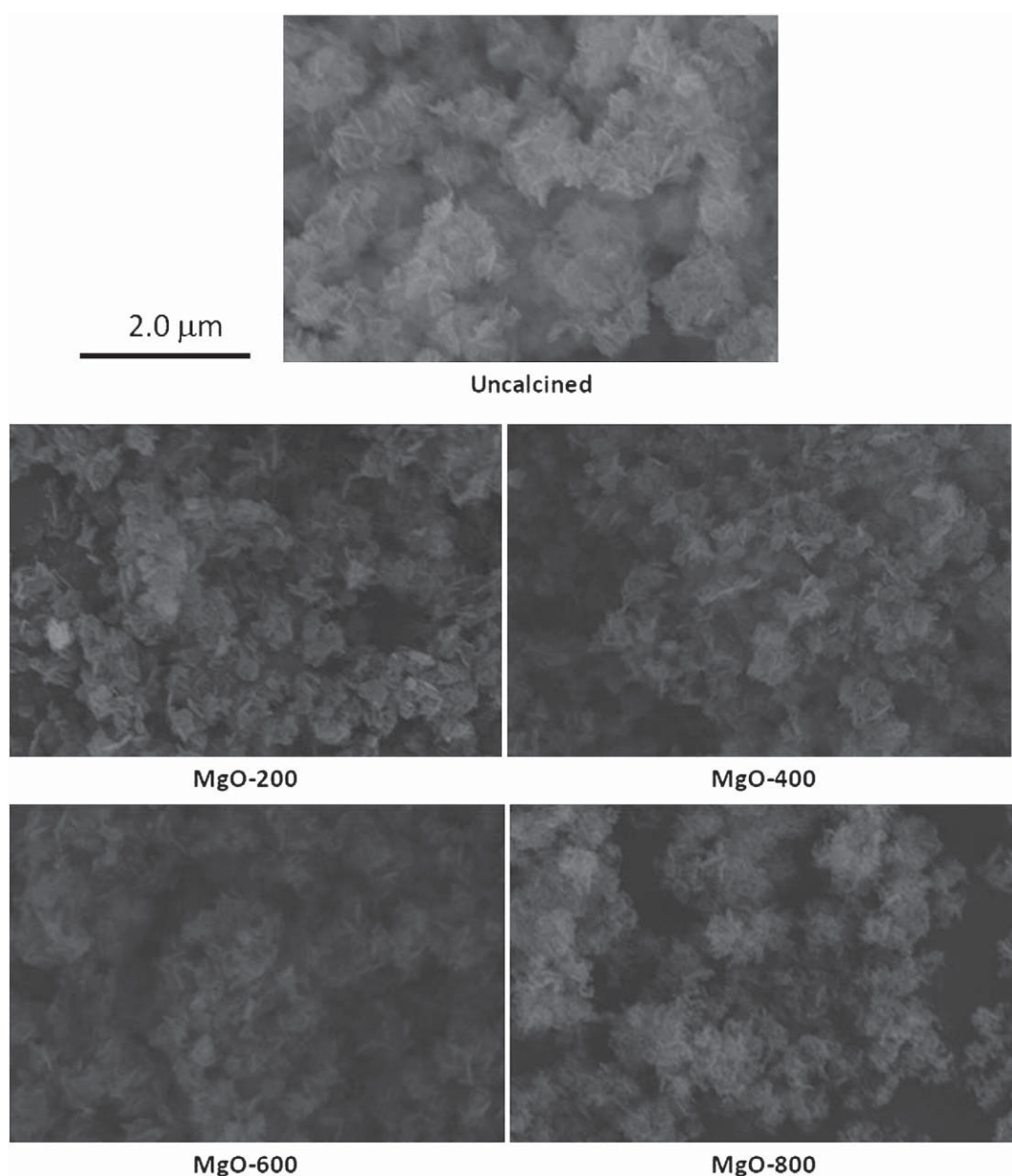


Fig. 2. The SEM micrographs of the Mg(OH)₂ and the MgO catalysts calcined at different temperatures.

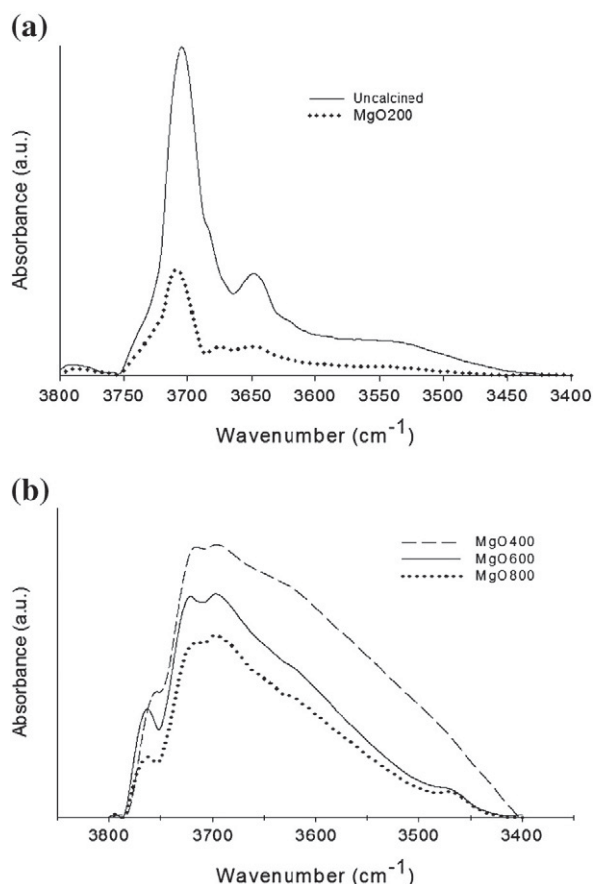


Fig. 3. The FT-IR spectra of MgO/Mg(OH)₂ calcined at various temperatures (a) Mg(OH)₂ phase, (b) MgO phase.

Fig. 5 shows the FT-IR results of the pre-adsorbed CO₂ at 100 °C on the various catalyst samples. According to the literature, the absorption bands in the 2000–2400 cm^{−1} region were assigned to the physisorbed and end-on chemisorbed CO₂ molecules [26,27] and the bands in the region below 1000 cm^{−1} were derived from an overtone of a fundamental lattice vibration of Mg–O stretching [28]. The Mg–O stretching bands were clearly observed for all the MgO samples calcined at 400 °C and higher, confirming the formation of MgO structure. In most of the *in-situ* IR studies of pre-adsorbed CO₂ at room temperature on MgO, bicarbonate, bidentate, and unidentate carbonate species were observed in the 1200–1700 cm^{−1} region [29].

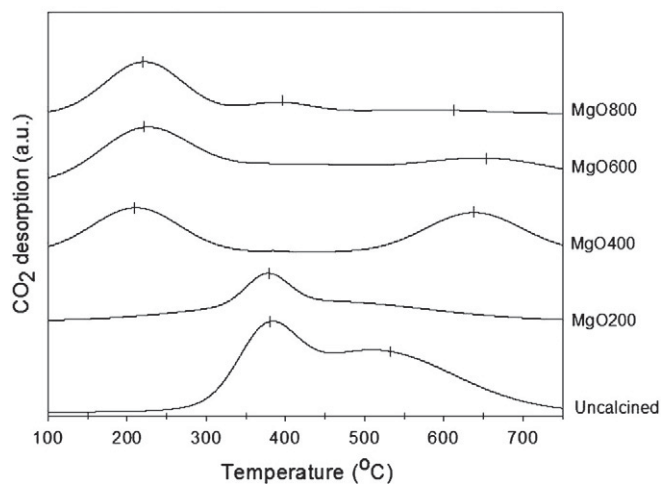


Fig. 4. The CO₂-TPD profiles of MgO/Mg(OH)₂ calcined at various temperatures.

Table 2

The amount of CO₂ desorption from CO₂-TPD profiles.

T _{calcined} (°C)	Amount of CO ₂ desorption (unit area/g)			
	1st peak	2nd peak	3rd peak	Total
Uncalcined	–	5.90	–	5.90
MgO200	–	2.46	–	2.46
MgO400	1.71	–	1.34	3.05
MgO600	1.82	–	0.91	2.73
MgO800	1.78	0.33	0.29	2.40

The bicarbonate is the most labile species and disappears after evacuation at 373 K while both the unidentate and bidentate carbonates remain on the surface after evacuation at 573 K. However, only the unidentate bands are observed upon evacuation at higher temperatures [29]. In the present work, the absorption at 1500–1506 cm^{−1} which was assigned to the unidentate species [27–29] was presented on the MgO catalysts and was found to be relatively more obvious on the MgO400. The results were correlated well with the CO₂-TPD results in which the MgO400 contained the highest amount of strong basic sites.

Fig. 6 shows the ESR results of the various MgO catalyst samples. There was almost no signal for the uncalcined catalyst and the MgO200. For those containing MgO crystalline phase (MgO400, MgO600, and MgO800), two signals of the g factor were observed. The sharp peak at g = 1.980 was assigned to the unpaired e[−] unstable oxygen radicals associated with lattice defects [30]. The broad one at g = 2.002 was assigned to one anion vacancies [31,32]. The intensity of both ESR signals increased with increasing calcination temperature.

The strength of basicity of the MgO and Mg(OH)₂ catalysts in this study was categorized into 3 types corresponding to the three desorption temperature ranges in the CO₂-TPD profiles, viz. 100–300 °C (weak basic sites), 300–550 °C (medium basic sites), and 550–750 °C (strong basic sites). It was found that the uncalcined sample and the MgO200 contained only the medium strength basic sites

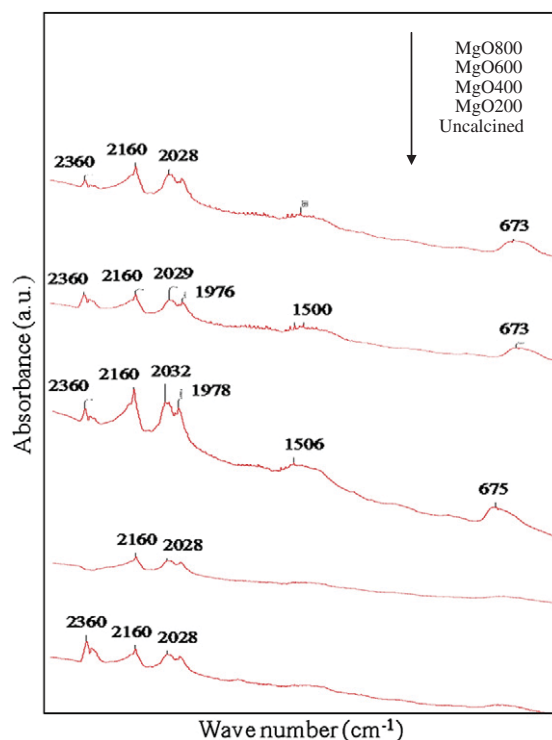


Fig. 5. The FT-IR spectra of pre-adsorbed CO₂ at 100 °C on the various MgO/Mg(OH)₂ catalysts.

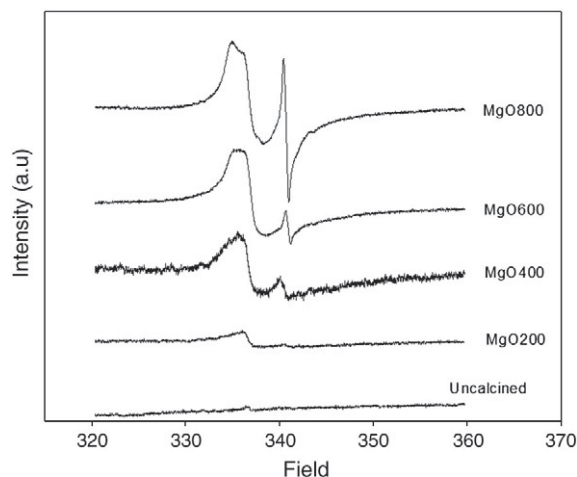


Fig. 6. The ESR spectra of MgO/Mg(OH)₂ calcined at various temperatures.

whereas the MgO400, MgO600, and MgO800 contained both weak and strong basic sites. The interactions of CO₂ with MgO surface sites have been investigated by Aramendia et al. [18] using *in-situ* IR measurements. Three kinds of adsorbed species were correlated to the different basic site strength: the unidentate carbonate forms on isolated surface O²⁻ ions, the bidentate carbonate forms on Lewis-acid–Brønsted-base pairs (Mg²⁺–O²⁻), and the bicarbonate species formation which involves surface hydroxyl groups. The strength order for surface basic sites was determined to be O²⁻ ions > oxygen in Mg–O pairs > OH groups. In the present study, the strong basic sites of MgO catalysts decreased significantly with increasing calcination temperature while the weak basic sites remained unaltered. The strong basic sites were correlated to the oxygen in Mg–O pairs because the more the lattice defects (as shown by increased ESR signals in Fig. 6), the lower the amount of strong basic sites. In other words, an increase of the calcination temperature gave rise to a significant reduction of lattice oxygen.

It has been reported that different types of OH groups were presented on the surface of magnesium oxide, which will not disappear completely at calcination temperatures below 900 °C [33]. Based on our FT-IR results, a sharp and intense –OH stretching vibration peak at 3700 cm⁻¹ indicated the presence of a hydroxyl group at the low-coordination sites in the Mg(OH)₂ structure [34] while smaller broad band peaks in the range of 3400–3750 cm⁻¹ were attributed to the isolated hydroxyl groups on the MgO samples [24,25]. It is likely that these OH groups contributed to the medium and the weak basic sites of Mg(OH)₂ and MgO, respectively. The different structures contributing to the basicity of MgO are illustrated in Fig. 7.

3.3. Isomerization of 1-butene

The activity and selectivity of the catalysts with different basic properties were investigated in the isomerization of 1-butene to 2-butene at 300 °C and ambient pressure. Fig. 8 shows the conversion of 1-butene as a function of time-on-stream obtained on the various

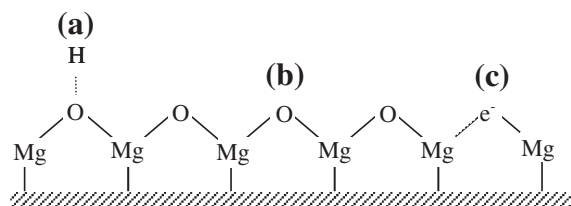


Fig. 7. The possible MgO structures contributing to the basicity (a) the isolated hydroxyl groups, (b) oxygen in MgO lattice, and (c) one anion vacancies.

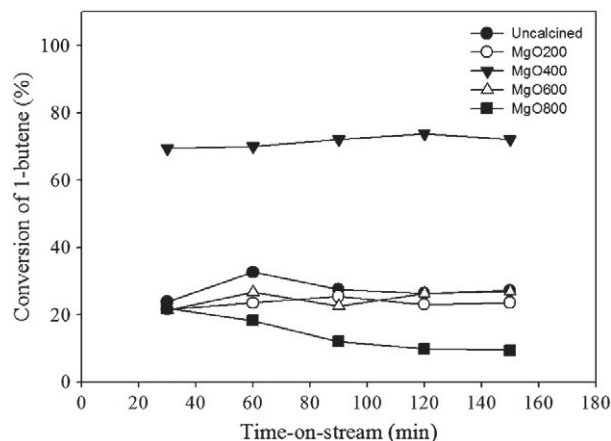


Fig. 8. Catalyst performances in the gas-phase isomerization of 1-butene to 2-butene at 300 °C.

catalysts. The 1-butene conversions were found to be in the order of MgO400 > MgO600 ≈ uncalcined catalyst > MgO200 > MgO800. The selectivity to 2-butene was more than 99% for all the catalysts under the reaction conditions used. There was no significant catalyst deactivation during the 150 min time-on-stream. The isomerization of 1-butene has been suggested to proceed via a carbanion intermediate on the strong basic sites [14] as illustrated in Scheme 1. The basic oxide ion facilitated the abstraction of an allylic proton and transferred to the terminal methyl group [7].

In the present study, we can divide the catalysts into two groups according to their structures: (1) the Mg(OH)₂ phase containing only medium strength basic sites (uncalcined catalyst and MgO200) and (2) the MgO crystalline phase (MgO400, MgO600, and MgO800) containing both weak and strong basic sites. For any surface catalytic reaction, high specific surface area available for adsorption of reactant is necessary. However, it appeared that the basicity of MgO and Mg(OH)₂ catalysts played a more decisive role in 1-butene isomerization reaction than the available surface area. For example, the BET surface area of MgO400 was twice that of MgO600 but the percent conversion of 1-butene obtained over the MgO400 catalyst was almost 3 times higher than that of MgO600. The MgO800 possessed BET surface area of 59 m²/g but exhibited very low conversion of 1-butene isomerization (ca. 9%) compared to the MgO600 with a BET surface area of 91 m²/g that exhibited 27% conversion of 1-butene.

The catalyst activity in 1-butene isomerization activity was found to be dependent not only on the amount of basic sites but also the distribution of basic strength. The MgO400 catalyst had the highest amount of strong basic sites and exhibited the highest isomerization activity. The MgO600 with less amounts of strong basic sites showed similar isomerization activity to that of the uncalcined catalyst containing only medium strength basic sites. Based on the CO₂ TPD results, there was no significant difference in the amount of weak basic sites on the various MgO catalysts, suggesting that the weak basic sites in MgO catalysts had little impact on the isomerization activity of MgO catalysts. Similar to the weak basic sites, the presence of the unpaired e⁻ unstable oxygen radicals did not promote the reaction. Considering the Mg(OH)₂ phase catalysts, the conversion of 1-butene was found to decrease with decreasing amount of the medium basic sites. It is proposed that the medium strength basic sites were also responsible for 1-butene isomerization. Moreover, the corner O²⁻ ions at low-coordination number have been proposed to be capable of abstracting an allylic hydrogen from 1-butene [13].

4. Conclusions

The co-precipitation of Mg(NO₃)₂·6H₂O and KOH resulted in the formation of Mg(OH)₂ with an average crystallite size of 17.4 nm and