รายงานวิจัยฉบับสมบูรณ์

โครงการ
การศึกษาโลหะออกไซด์ผสมสามองค์ประกอบเป็นตัวเร่งปฏิกิริยาวิวิธพันธุ์ชนิดเบสสำหรับการสังเคราะห์โอเลโอเคมิคอล

โดย

ผู้ช่วยศาสตราจารย์ ดร.ชวลิต งามจรัสศรีวิชัย

ภาควิชาเคมีเทคนิค คณะวิทยาศาสตร์

จุฬาลงกรณ์มหาวิทยาลัย

มีนาคม 2554

สัญญาเลขที่ MRG5280113

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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

บทคัดย่อ

รหัสโครงการ : MRG5280113

ชื่อโครงการ : การศึกษาโลหะออกไซด์ผสมสามองค์ประกอบเป็นตัวเร่งปฏิกิริยาวิวิธพันธุ์ชนิดเบสสำหรับการสังเคราะห์โอเลโอเคมิคอล

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ระยะเวลาโครงการ : 2 ปี

โครงการวิจัยนี้ศึกษาการเตรียมและการวิเคราะห์ลักษณะสมบัติของโลหะออกไซด์ผสมของแคลเซียมเพื่อใช้เป็นตัวเร่งปฏิกิริยาวิวิธพันธุ์ชนิดเบสสำหรับทรานส์เอสเทอริฟิเคชันของน้ำมันเมล็ดในปาล์มกับเมทานอลที่อุณหภูมิ 60 องศาเซลเซียสและความดัน 1 บรรยากาศ โดยงานวิจัยแบ่งออกเป็น 2 ส่วนตามวิธีการเตรียมตัวเร่งปฏิกิริยา ได้แก่ 1) ตัวเร่งปฏิกิริยาที่เตรียมจากการเผาสารประกอบแคลเซียมธรรมชาติ เช่น แคลไซต์ โดโลไมต์ ไฮดรอกซีอะพาไทต์ กระดองปลาหมึก เป็นต้น ที่อุณหภูมิ 600-900 องศาเซลเซียส และ 2) ตัวเร่งปฏิกิริยาที่เตรียมจากการตกตะกอนร่วมสารละลายแคลเซียมที่ผสมกับโลหะอื่นอีกสองชนิด ได้แก่ Mg, Ba, Zn และ Al การวิเคราะห์ลักษณะสมบัติของตัวเร่งปฏิกิริยาที่เตรียมได้ใช้เทคนิคต่างๆ ได้แก่ powder X-ray diffraction (XRD), N_2 adsorption-desorption measurement, thermogravimetric/differential thermal analysis (TG/DTA), X-ray fluorescence spectroscopy (XRF), scanning electron microscopy (SEM) และ temperature-programmed desorption (TPD) ของ CO_2 จากการศึกษาพบว่า โดโลไมต์ที่ผ่านการเผาที่อุณหภูมิ 800 องศาเซลเซียส เป็นตัวเร่งปฏิกิริยาที่ให้ผลได้ของเมทิลเอสเทอร์สูงสุดในกลุ่มของแคลเซียมธรรมชาติ ขณะที่ออกไซด์ผสมของ CaMgZn เป็นตัวเร่งปฏิกิริยาที่ว่องไวที่สุดในกลุ่มของตัวเร่งปฏิกิริยาที่เตรียมผ่านการตกตะกอนร่วม ความสามารถในการเร่งปฏิกิริยาสัมพันธ์อย่างยิ่งกับปริมาณตำแหน่งเบส CaO เป็นตำแหน่งเบสที่ว่องไวสำหรับทรานส์เอสเทอริฟิเคชันของน้ำมันเมล็ดในปาล์มกับเมทานอล อัตราส่วนโดยโมลของคาร์บอเนตต่อไฮดรอกไซด์ (CO_3^{2-}/OH^-) และอุณหภูมิในการเผาตะกอนเป็นปัจจัยที่สำคัญในการเตรียมตัวเร่งปฏิกิริยาโลหะออกไซด์ผสม CaMgZn ที่มีความว่องไวสูง

คำหลัก : ไบโอดีเซล ทรานส์เอสเทอริฟิเคชัน ตัวเร่งปฏิกิริยาวิวิธพันธุ์ โลหะออกไซด์ผสม

ABSTRACT

Project Code : MRG5280113

Project Title : Study on three-component mixed oxides as heterogeneous base catalysts for synthesis of oleochemicals

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Project Period : 2 years

The present project has investigated preparation and characterization of Ca-based mixed metal oxides as heterogeneous base catalysts for transesterification of palm kernel oil with methanol at 60 $^{\circ}$C and 1 atm. The study was divided into 2 parts according to the catalyst preparation methods; 1) The catalysts attained by calcination of natural calcium compounds at temperatures between 600 and 900 $^{\circ}$C and 2) the catalysts prepared by precipitation of a solution of Ca mixed with other two metals selected from Mg, Ba, Zn and Al. The characterization of the catalysts was carried out by using several techniques, including powder X-ray diffraction (XRD), N_2 adsorption-desorption measurement, thermogravimetric/differential thermal analysis (TG/DTA), X-ray fluorescence spectroscopy (XRF), scanning electron microscopy (SEM) and temperature-programmed desorption (TPD) of CO_2. It was found that, for the natural calcium compounds, dolomite calcined at 800 $^{\circ}$C gave the highest yield of methyl esters. On the other hand, the mixed oxide of Ca, Mg and Zn (CaMgZn) was the most active catalyst synthesized by the co-precipitation method. The catalytic performance was strongly dependent on the amount of basic sites. CaO was catalytically active site responsible for the transesterification of palm kernel oil with methanol. The molar ratio of CO_3^{2-}/OH^- and the calcination temperature for the precipitate were important parameters for the preparation of highly active CaMgZn mixed oxide.

Keywords : Biodiesel, Transesterification, Heterogeneous catalysts, Mixed metal oxides

สรุปย่อ

EXECUTIVE SUMMARY

ในการดำเนินโครงการเป็นระยะเวลา 2 ปี ผู้วิจัยได้ศึกษาการเตรียมและการวิเคราะห์ลักษณะสมบัติของโลหะออกไซด์ผสมของแคลเซียมเพื่อใช้เป็นตัวเร่งปฏิกิริยาวิวิธพันธุ์ชนิดเบสสำหรับทรานส์เอสเทอริฟิเคชันของน้ำมันเมล็ดในปาล์มกับเมทานอลเพื่อผลิตเมทิลเอสเทอร์ซึ่งสามารถใช้เป็นเชื้อเพลิงหรือสารหล่อลื่น (lubricant) ได้ โดยมีเป้าหมายพัฒนาตัวเร่งปฏิกิริยาโลหะออกไซด์ผสมของแคลเซียมที่มีความว่องไวสูง สามารถนำกลับมาใช้ได้หลายครั้ง และมีราคาถูก

การเตรียมตัวเร่งปฏิกิริยาแบ่งออกเป็น 2 วิธี ได้แก่ 1) การเผาสารประกอบแคลเซียมธรรมชาติที่ผ่านการบดและคัดขนาดแล้ว ได้แก่ แคลไซต์ (calcite) โดโลไมต์ (dolomite) ไฮดรอกซีอะพาไทต์ (hydroxyapatite) ไดไฮโดรเจนฟอสเฟต (dihydrogen phosphate) และกระดองปลาหมึก (cuttlebone) ที่อุณหภูมิในช่วง 600-900 องศาเซลเซียส โดยศึกษาผลของโครงสร้างของแคลเซียมธรรมชาติและอุณหภูมิในการเผา และผลของภาวะในการทำทรานส์เอสเทอริฟิเคชันที่มีต่อผลได้ (yield) ของเมทิลเอสเทอร์ และ 2) การตกตะกอนสารละลายของแคลเซียมผสมกับโลหะอื่นอีกสองชนิดที่เลือกจาก Mg, Ba, Zn และ Al โดยใช้โซเดียมคาร์บอเนต (Na_2CO_3) หรือแอมโมเนียคาร์บอเนต ($(NH_4)_2CO_3$) เป็นสารตกตะกอน (precipitant) การตกตะกอนทำที่อุณหภูมิและความดันบรรยากาศจากนั้นจึงนำไปบ่มต่อที่อุณหภูมิ 60 องศาเซลเซียส เป็นเวลา 8-20 ชั่วโมง โดยศึกษาปัจจัยต่างๆ ที่มีผลต่อผลได้ของเมทิลเอสเทอร์ ได้แก่ ชนิดของโลหะ ชนิดของสารตกตะกอน อัตราส่วนโดยโมลของคาร์บอเนตต่อไฮดรอกไซด์ (CO_3^{2-}/OH^-) และอุณหภูมิในการเผาตะกอน ทรานส์เอสเทอริฟิเคชันของน้ำมันเมล็ดในปาล์มกับเมทานอลทำในระบบแบตช์ที่อุณหภูมิ 60 องศาเซลเซียสและความดัน 1 บรรยากาศ โดยใช้อัตราส่วนโดยโมลของเมทานอลต่อน้ำมันเท่ากับ 15-30 ปริมาณตัวเร่งปฏิกิริยา 5-10 % และระยะเวลา 3-5 ชั่วโมง

โดโลไมต์ที่ผ่านการเผาที่อุณหภูมิ 800 องศาเซลเซียส เป็นเวลา 2 ชั่วโมง เป็นตัวเร่งปฏิกิริยาที่ให้ผลได้ของเมทิลเอสเทอร์สูงสุด (มากกว่า 98 %) จากผลการวิเคราะห์ลักษณะสมบัติด้วยเทคนิคต่างๆ ชี้ให้เห็นว่า การอยู่ร่วมกันของ Ca และ Mg ในรูปคาร์บอเนตผสม ($CaMg(CO_3)_2$) ช่วยลดอุณหภูมิที่ใช้ในการสลายหมู่คาร์บอเนตและการเกิดเป็นโลหะออกไซด์ผสม การเผาโดโลไมต์ที่อุณหภูมิ 800 องศาเซลเซียส ทำให้สารประกอบคาร์บอเนตผสมแปรสภาพเป็นออกไซด์และทำให้สมบัติความพรุน (textural properties) ของโดโลไมต์เพิ่มขึ้น การวิเคราะห์การกระจายผลิตภัณฑ์ (product distribution) ในทรานส์เอสเทอริฟิเคชันที่เวลาต่างๆ ทำให้ทราบว่า กลไกการเร่งปฏิกิริยาบนโลหะออกไซด์ผสมจากโดโลไมต์คล้ายคลึงกับการเร่งปฏิกิริยาแบบเอกพันธุ์

ตัวเร่งปฏิกิริยาที่เตรียมด้วยวิธีการตกตะกอนร่วมประกอบด้วย CaMgBa, CaMgZn, CaMgAl, CaBaZn, CaBaAl และ CaZnAl โดย CaMgZn และ CaBaZn เป็นตัวเร่งปฏิกิริยาที่ว่องไวมากที่สุด ให้ผลได้ของเมทิลเอสเทอร์มากกว่า 95 % งานวิจัยในส่วนนี้ไม่พบความสัมพันธ์ของพื้นที่ผิวจำเพาะและขนาดอนุภาคกับความสามารถในการเร่งทรานส์เอสเทอริฟิเคชันของตัวเร่งปฏิกิริยา แต่ความว่องไวใน

การเร่งปฏิกิริยาจะเพิ่มขึ้นเมื่อปริมาณของแคลเซียมมากขึ้น นอกจากนั้นพบการชะละลายของโลหะที่เป็นองค์ประกอบบางส่วนในเมทานอลด้วย จากการศึกษาจลนพลศาสตร์ (kinetics) เปรียบเทียบระหว่าง CaMgZn และ CaBaZn พบว่า CaMgZn เร่งทรานส์เอสเทอริฟิเคชันได้ว่องไวกว่า CaBaZn ซึ่งน่าจะเกิดจากปริมาณตำแหน่งเบสรวมของ CaMgZn สูงกว่า CaBaZn

จากการศึกษาการนำโลหะออกไซด์ผสม CaMgZn กลับมาใช้ใหม่ (reusability) และการฟื้นฟูสภาพ (regeneration) พบว่า เกิดการเสื่อมสภาพของตัวเร่งปฏิกิริยา ซึ่งอาจเกิดจากกลีเซอรอลที่เป็นผลิตภัณฑ์ข้างเคียงในทรานส์เอสเทอริฟิเคชันทำปฏิกิริยากับ CaO และเกิดเป็นแคลเซียมกลีเซอรอไซด์ (calcium glyceroxide, $Ca(O_3H_7C_3)_2$) ซึ่งจะปกคลุมผิวหน้าของตัวเร่งปฏิกิริยาไว้ทำให้ปฏิกิริยาเกิดได้น้อยลง การล้างด้วยตัวทำละลายที่มีน้ำเป็นองค์ประกอบ ได้แก่ สารละลายแอมโมเนียมไฮดรอกไซด์ จะทำให้แคลเซียมกลีเซอรอไซด์เกิดไฮโดรไลซิสและได้ CaO กลับมาเร่งปฏิกิริยาได้ใกล้เคียงเดิม

เนื้อหางานวิจัย

โครงการวิจัยนี้แบ่งออกเป็น 2 ส่วนตามวิธีการเตรียมตัวเร่งปฏิกิริยา ได้แก่ 1) ตัวเร่งปฏิกิริยาที่ได้จากการเผาสารประกอบแคลเซียมธรรมชาติ ได้แก่ แคลไซต์ (calcite) โดโลไมต์ (dolomite) ไฮดรอกซีอะพาไทต์ (hydroxyapatite) ไดไฮโดรเจนฟอสเฟต (dihydrogen phosphate) และกระดองปลาหมึก (cuttlebone) ที่อุณหภูมิ 600-900 องศาเซลเซียส และ 2) ตัวเร่งปฏิกิริยาที่เตรียมจากการตกตะกอนร่วมสารละลายแคลเซียมที่ผสมกับโลหะอื่นอีกสองชนิด ได้แก่ Mg, Ba, Zn และ Al และผ่านการเผาที่อุณหภูมิในช่วง 600-900 องศาเซลเซียส

1. แคลเซียมธรรมชาติ (Natural calcium)

1.1 การเตรียมตัวเร่งปฏิกิริยาโลหะออกไซด์จากแคลเซียมธรรมชาติ

แคลไซต์ ($CaCO_3$) และโดโลไมต์ ($CaMg(CO_3)_2$) ได้รับความอนุเคราะห์จาก บริษัท ไทยโดโลไมต์ จำกัด จังหวัดสุราษฎร์ธานี กระดองปลาหมึกที่ใช้ในงานนี้ได้จากหมึกกล้วย (splendid squid) *Loligo formosana* Sasaki ซึ่งเป็นสายพันธุ์ที่พบมากที่สุดสายพันธุ์หนึ่งในอ่าวไทย จากการวิเคราะห์องค์ประกอบธาตุด้วยเทคนิค XRF พบว่า แคลไซต์และกระดองปลาหมึกมี $CaCO_3$ เป็นองค์ประกอบมากกว่า 91 % โดยน้ำหนัก ขณะที่โดโลไมต์ประกอบด้วย CaO 16.56 %, MgO 31.20 %, Fe_2O_3 298 ppm, SrO 198 ppm และที่เหลือเป็น CO_2 ไฮดรอกซีอะพาไทต์ ($Ca(PO_4)_6(OH)_2$) และไดไฮโดรเจนฟอสเฟต เป็นเกรดสารเคมี (AR grade) จากบริษัท Ajax Finechem ก่อนนำวัสดุเหล่านี้มาใช้เป็นตัวเร่งปฏิกิริยาจะทำการบดและคัดขนาดให้เล็กกว่า 10 ไมครอน จากนั้นนำไปเผาที่อุณหภูมิในช่วง 600-900 องศาเซลเซียส

1.2 การวิเคราะห์ลักษณะสมบัติของโลหะออกไซด์ที่เตรียมได้จากแคลเซียมธรรมชาติ

การวิเคราะห์ลักษณะสมบัติของวัสดุแคลเซียมธรรมชาติและโลหะออกไซด์ที่ได้ใช้เทคนิคต่างๆ ดังต่อไปนี้

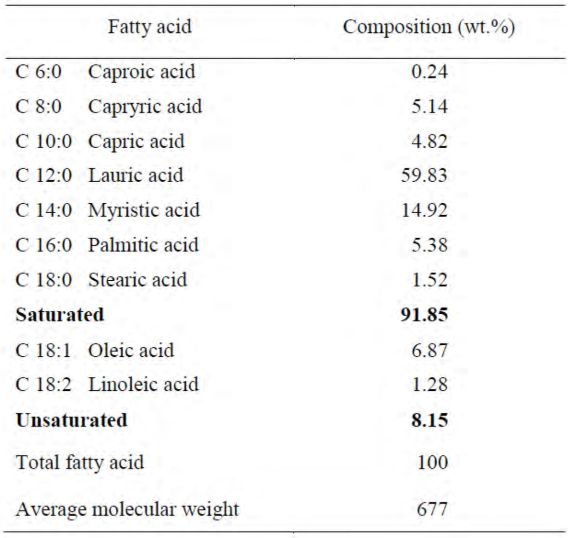
ลักษณะสมบัติ	เทคนิคในการวิเคราะห์
โครงสร้างและความเป็นผลึกของออกไซด์	Powder X-ray diffraction (XRD) using a Bruker D8 ADVANCE diffractometer
พื้นที่ผิวจำเพาะ (specific surface area) ขนาดรูพรุน (pore size) และปริมาตรรูพรุน (pore volume)	Nitrogen adsorption-desorption measurement using a Micromeritics ASAP 2000 surface area and porosity analyzer
การสลายตัวขององค์ประกอบตัวเร่งปฏิกิริยา	Thermogravimetric analysis (TGA) using a Perkin Elmer Pyris Diamond thermogravimetry (TG/DTA)

องค์ประกอบธาตุ	X-ray fluorescence spectroscopy (XRF) using an Oxford ED-2000 energy dispersive X-ray fluorescence spectrometer
ขนาดอนุภาค (particle size) และสัณฐาน (morphology)	Scanning electron microscopy (SEM) using a JEOL JSM-5800LV scanning electron microscope
สมบัติความเป็นเบส	Temperature-programmed desorption of CO_2 using a Micromeritics Autochem II chemisorption analyzer

1.3 การทดสอบความสามารถในการเร่งปฏิกิริยาทรานส์เอสเทอริฟิเคชันของน้ำมันพืชกับเมทานอล

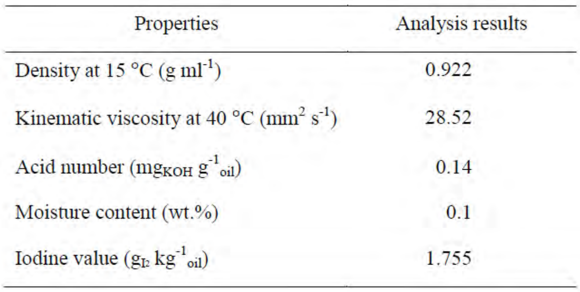
การศึกษาการเร่งปฏิกิริยาทรานส์เอสเทอริฟิเคชันทำในขวดก้นกลมสามคอปริมาตร 100 มิลลิลิตร ซึ่งต่อเข้ากับคอนเดนเซอร์ ควบคุมอุณหภูมิด้วยอ่างควบคุมอุณหภูมิ (water bath) ทำการกวนด้วยเครื่องกวนแม่เหล็ก น้ำมันเริ่มต้นที่ใช้ในการผลิตไบโอดีเซลคือ น้ำมันเมล็ดในปาล์มที่ผ่านการกลั่นแล้ว (refined palm kernel oil, PKO) จากบริษัท ชุมพรอุตสาหกรรมน้ำมันปาล์ม จำกัด (มหาชน) กรดไขมันที่เป็นองค์ประกอบและสมบัติเบื้องต้นของ PKO แสดงในตารางที่ 1 และ 2 ตามลำดับ

ตารางที่ 1 องค์ประกอบกรดไขมันของน้ำมันเมล็ดในปาล์ม



Fatty acid	Composition (wt.%)
C 6:0 Caproic acid	0.24
C 8:0 Capryric acid	5.14
C 10:0 Capric acid	4.82
C 12:0 Lauric acid	59.83
C 14:0 Myristic acid	14.92
C 16:0 Palmitic acid	5.38
C 18:0 Stearic acid	1.52
Saturated	**91.85**
C 18:1 Oleic acid	6.87
C 18:2 Linoleic acid	1.28
Unsaturated	**8.15**
Total fatty acid	100
Average molecular weight	677

ตารางที่ 2 สมบัติของกรดไขมันของน้ำมันเมล็ดในปาล์ม

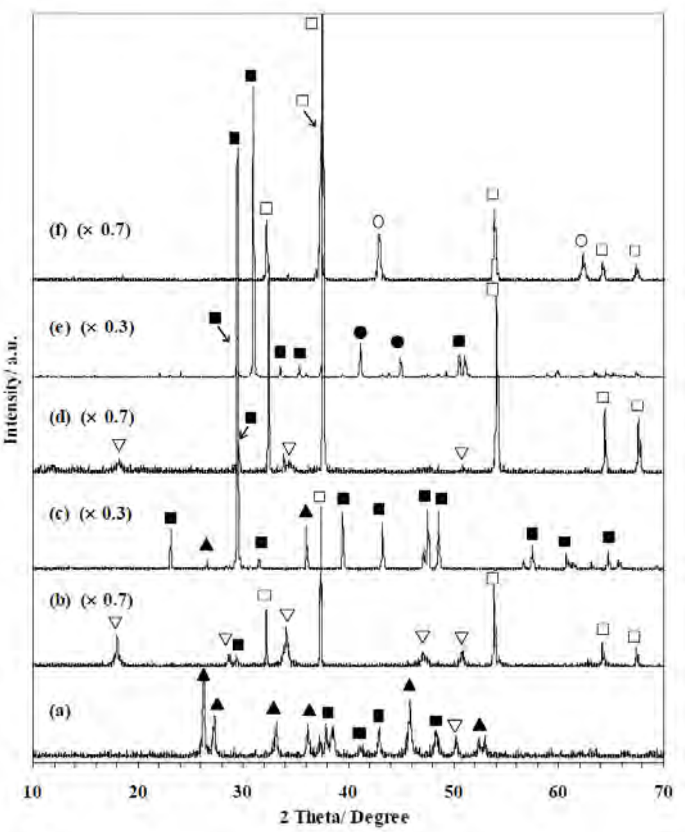


Properties	Analysis results
Density at 15 °C (g ml^{-1})	0.922
Kinematic viscosity at 40 °C (mm^2 s^{-1})	28.52
Acid number (mg$_{KOH}$ g^{-1}$_{oil}$)	0.14
Moisture content (wt.%)	0.1
Iodine value (g$_{I_2}$ kg^{-1}$_{oil}$)	1.755

ส่วนแอลกอฮอล์ที่ใช้คือ เมทานอลเกรดการค้า (99%) อุณหภูมิของปฏิกิริยาตั้งไว้ที่ 60 องศาเซลเซียส และอัตราเร็วในการกวนเป็น 500 รอบต่อนาทีโดยประมาณ ทำการแปรเปลี่ยนอัตราส่วนโดยโมลของเมทานอลต่อน้ำมันในช่วง 10-50 ปริมาณตัวเร่งปฏิกิริยา 0.5-10 % และเวลาทำปฏิกิริยาในช่วง 30-180 นาที ภายหลังเสร็จสิ้นปฏิกิริยา แยกตัวเร่งปฏิกิริยาออกด้วยเครื่องปั่นเหวี่ยง (centrifuge) กำจัดเมทานอลที่มากเกินพอออกด้วยเครื่องระเหยแบบหมุน (rotary evaporator) แยกกลีเซอรอลออกและล้างชั้นเมทิลเอสเทอร์ด้วยน้ำกลั่น จากนั้นนำชั้นเมทิลเอสเทอร์ไปทำให้แห้งด้วยโซเดียมซัลเฟต

วิเคราะห์หาปริมาณเมทิลเอสเทอร์ในผลิตภัณฑ์ที่ได้ด้วยเครื่องแก๊สโครมาโตกราฟ ยี่ห้อ Varian รุ่น CP3800 ดีเทคเตอร์ชนิด FID และคอลัมน์ชนิด DB-Wax และวิเคราะห์หาปริมาณของกลีเซอไรด์ด้วยเครื่องแก๊สโครมาโตกราฟ ยี่ห้อ Agilent Technology ดีเทคเตอร์ชนิด FID และคอลัมน์ชนิด DB-1ht

1.4 ผลงานวิจัยที่ได้รับ



รูปที่ 1 XRD patterns of non-calcined cuttlebone (a), cuttlebone calcined at 800 °C, 2 h (b), non-calcined calcite (c), calcite calcined at 800 °C, 2 h (d), non-calcined dolomite (e), and dolomite calcined at 800 °C, 2 h (f). (Symbols: ▲ = aragonite $CaCO_3$, ■ = calcite $CaCO_3$, ● = $MgCO_3$, □ = CaO, ○ = MgO and ▽ = $Ca(OH)_2$)

รูปที่ 1 แสดงรูปแบบ XRD ของกระดองปลาหมึก แคลไซต์ และโดโลไมต์ก่อนและหลังการเผาที่อุณหภูมิ 800 องศาเซลเซียส ก่อนการเผา $CaCO_3$ ในกระดองปลาหมึกอยู่ในรูปของ aragonite ซึ่งมีโครงสร้างผลึกแบบ orthorhombic ขณะที่แคลไซต์มี $CaCO_3$ ที่มีโครงสร้างผลึกเป็น rhombohedral หลังการเผาวัสดุแคลเซียมธรรมชาติทั้งสองชนิดจะมี CaO ที่มีโครงสร้างผลึกแบบ cubic เป็นหลัก อย่างไรก็ดี $CaCO_3$ (2θ = 29.4°) ยังคงเหลืออยู่ ส่วนโดโลไมต์ซึ่งเป็น $CaCO_3$ และ $MgCO_3$ จะไม่พบสารประกอบคาร์บอเนตเหลืออยู่หลังการเผา ผลการทดลองนี้ชี้ให้เห็นว่า การเป็นคาร์บอเนตผสมของ Ca และ Mg ช่วยสนับสนุน decarbonation ของโดโลไมต์ สำหรับสัญญาณ $Ca(OH)_2$ ที่พบน่าจะเกิดจากการแปรสภาพของ CaO เมื่อสัมผัสกับความชื้นในอากาศ งานวิจัยก่อนหน้านี้แสดงให้เห็นว่าการเกิดเป็น $Ca(OH)_2$ ทำให้ความสามารถในการเร่งปฏิกิริยาของ CaO ลดลงอย่างมาก

ตารางที่ 3 แสดงปริมาณของเมทิลเอสเทอร์ที่สังเคราะห์ได้จากทรานส์เอสเทอริฟิเคชันของ PKO กับเมทานอลด้วยตัวเร่งปฏิกิริยาแคลเซียมชนิดต่างๆ หลังการเผาที่อุณหภูมิ 800 องศาเซลเซียส ซึ่งจะเห็นได้ว่า โดโลไมต์เร่งทรานส์เอสเทอริฟิเคชันได้สูงกว่าแคลไซต์ กระดองปลาหมึก ไฮดรอกซีอะพาไทต์ และไดไฮโดรเจนฟอสเฟต จากการเปรียบเทียบการเร่งปฏิกิริยาด้วย CaO และ MgO เกรดการค้าสะท้อนให้เห็นว่า CaO ในโดโลไมต์เป็นตำแหน่งเบสที่ว่องไวสำหรับทรานส์เอสเทอริฟิเคชันของ PKO

ผลของอุณหภูมิในการเผาโดโลไมต์ที่มีต่อผลได้ของเมทิลเอสเทอร์แสดงในตารางที่ 4 ซึ่งจะเห็นว่า อุณหภูมิในการเผาเท่ากับ 800 องศาเซลเซียส เป็นอุณหภูมิที่เหมาะสมในการเตรียมตัวเร่งปฏิกิริยาจากโดโลไมต์ จากผลการวิเคราะห์โครงสร้างของโดโลไมต์ที่ผ่านการเผาที่อุณหภูมิต่างๆ พบว่าอุณหภูมิที่ต่ำกว่า 800 องศาเซลเซียส ไม่สามารถสลายสารประกอบคาร์บอเนตเพื่อเปลี่ยนเป็นออกไซด์

ได้ ขณะที่อุณหภูมิที่ 900 องศาเซลเซียส จะทำให้ CaO มีขนาดผลึกที่ใหญ่ขึ้น ซึ่งอาจเกิดจากการหลอมรวม (sintering) ของ CaO และน่าจะมีผลต่อพื้นที่ผิวจำเพาะ

ตารางที่ 3 Transesterification of PKO over various calcium compounds calcined at 800 °C

Catalyst	Methyl ester content (wt.%)
Calcite	46.8
Cuttlebone	24.1
Hydroxyapatite	2.6
Dicalcium phosphate	1.3
Dolomite	98.6
CaO	92.8
$MgCO_3$	1.2
MgO	0.7

Reaction conditions: catalyst amount, 6 wt.%; methanol/oil, 30; temperature, 60 °C, time, 3 h.

ตารางที่ 4 Transesterification of PKO over dolomites calcined at different calcination temperatures

Calcination temperature (°C)	Methyl ester content (wt.%)
600	0.0
700	0.0
800	98.6
900	81.2

Reaction conditions: catalyst amount, 6 wt.%; methanol/oil, 30; temperature, 60 °C, time, 3 h.

ตารางที่ 5 แสดงผลการวิเคราะห์พื้นที่ผิวจำเพาะ ปริมาตรรูพรุน และขนาดรูพรุนของโดโลไมต์ที่ผ่านการเผาที่อุณหภูมิต่าง ๆ การเพิ่มอุณหภูมิในการเผาทำให้พื้นที่ผิวจำเพาะและปริมาตรรูพรุนของโดโลไมต์เพิ่มขึ้น แต่การเพิ่มอุณหภูมิในการเผาสูงกว่า 800 องศาเซลเซียส ทำให้สมบัติความพรุนของโดโลไมต์ลดลง ซึ่งผลการวิเคราะห์ที่ได้สอดคล้องกับภาพถ่าย SEM ที่พื้นผิวของโดโลไมต์ (รูปที่ 2) ซึ่งจะเห็นได้ว่า โดโลไมต์เผาที่ 900 องศาเซลเซียส จะพบรอยแตกเกิดขึ้นที่พื้นผิวด้วย

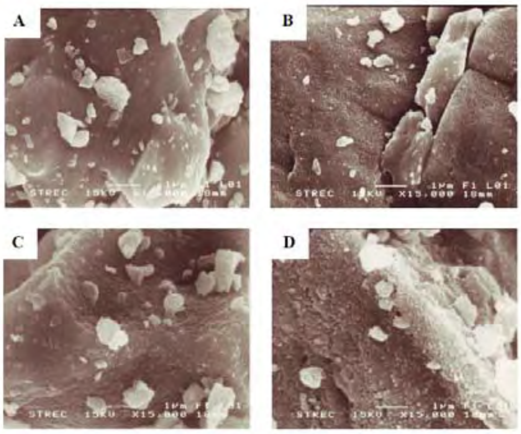
ตารางที่ 5 Textural properties of dolomites calcined at various temperatures

Calcination temperature (°C)	S_{BET}^{a} ($m^2 g^{-1}$)	V_p^{b} ($cm^3 g^{-1}$)	D_p^{c} (Å)
Before calcination	0.45	0.002	181.9
600	0.80	0.008	222.1
700	1.87	0.009	202.2
800	19.58	0.106	214.8
900	19.04	0.063	145.4

[a] BET surface area.

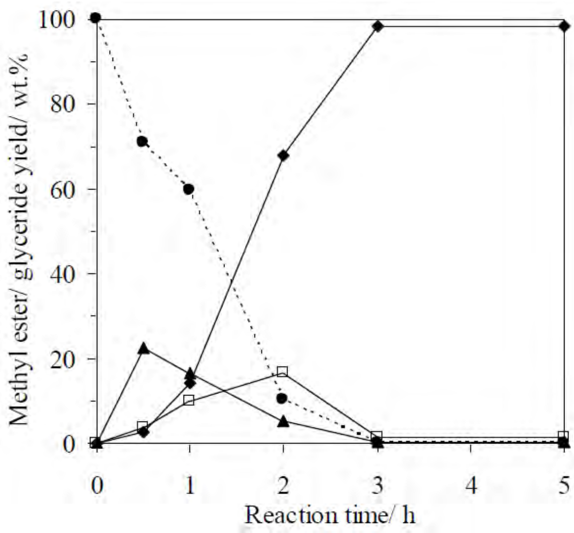
[b] Average pore volume.

[c] Average pore diameter.



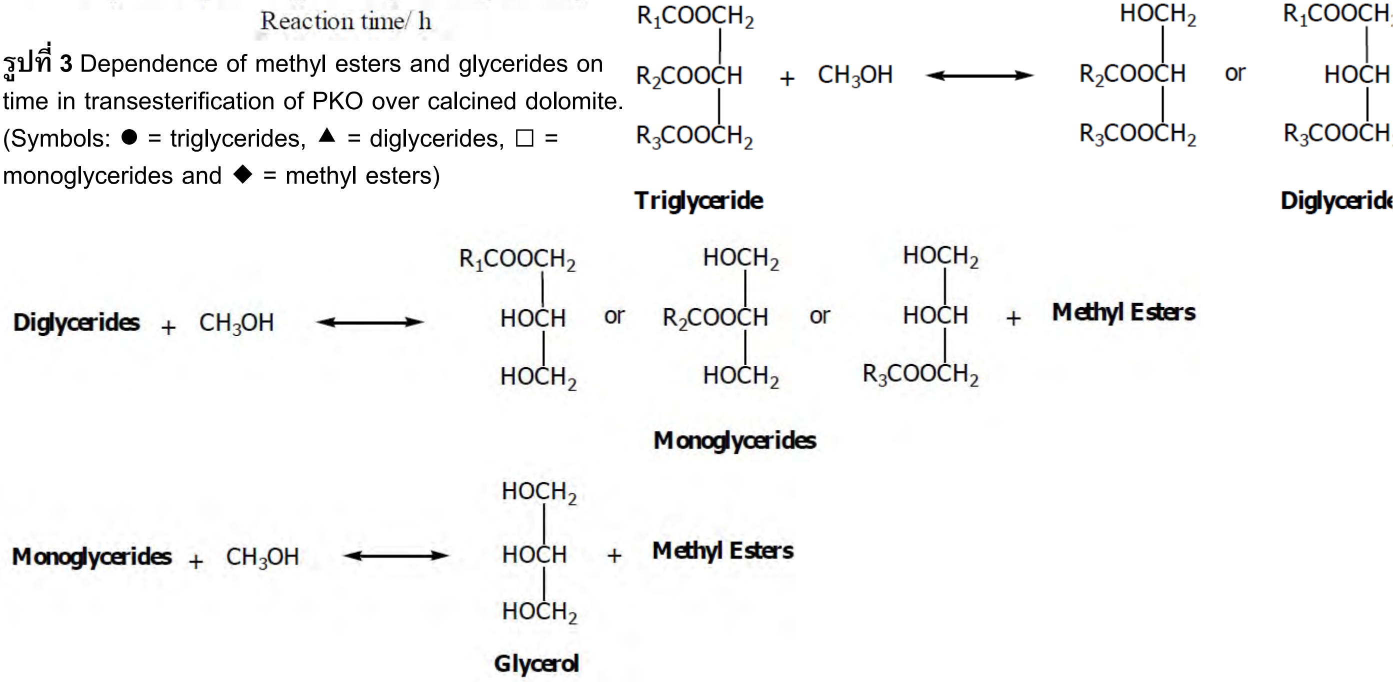
รูปที่ 2 SEM images of dolomites before calcination (A) and after calcination at 700 (B), 800 (C) and 900 (D) °C.

จากรูปที่ 3



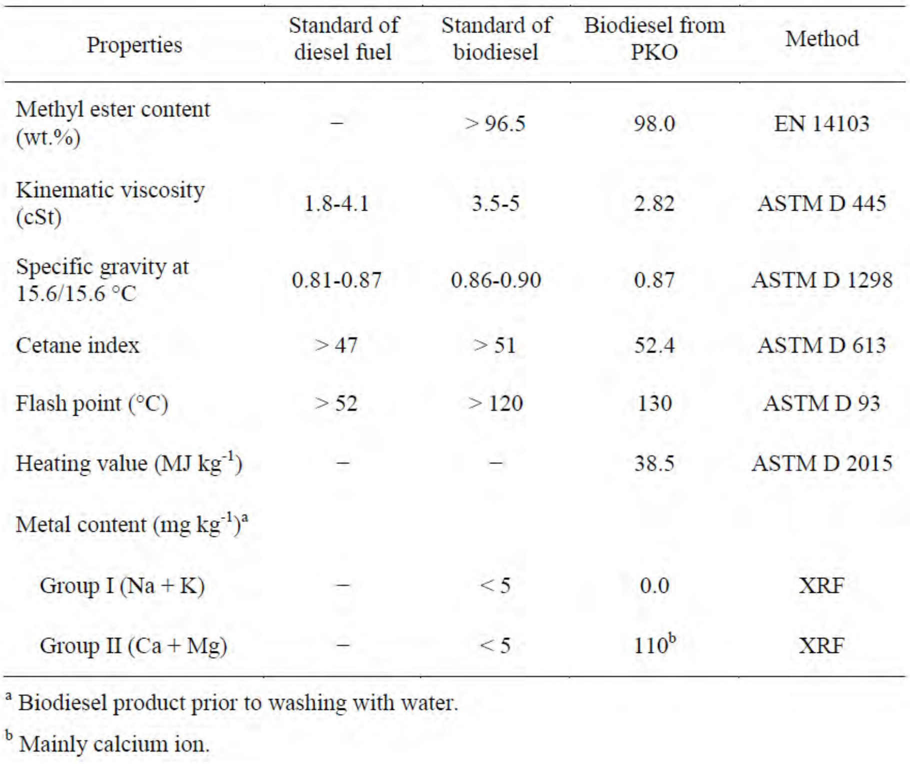
รูปที่ 3 Dependence of methyl esters and glycerides on time in transesterification of PKO over calcined dolomite. (Symbols: ● = triglycerides, ▲ = diglycerides, □ = monoglycerides and ◆ = methyl esters)

จนถึงชั่วโมงที่ 5 ของปฏิกิริยา นอกจากนั้น การกระจายของผลิตภัณฑ์ที่ได้มีความคล้ายคลึงกับการเร่งทรานส์เอสเทอริฟิเคชันของไตรกลีเซอไรด์ของน้ำมันพืชด้วยตัวเร่งปฏิกิริยาเบสแบบเอกพันธุ์ เช่น NaOH, KOH, $NaOCH_3$ เป็นต้น แสดงว่ากลไกการเร่งปฏิกิริยาแบบเอกพันธุ์และวิวิธพันธุ์มีความคล้าย คลึงกัน



ตารางที่ 6 แสดงการเปรียบเทียบสมบัติทางเชื้อเพลิงที่สำคัญบางประการของไบโอดีเซลที่ผลิตจาก PKO และเมทานอลกับมาตรฐานไบโอดีเซลและน้ำมันดีเซลที่กรมธุรกิจพลังงาน กระทรวงพลังงานกำหนด ไบโอดีเซลที่ผลิตจากงานวิจัยนี้มีสมบัติผ่านมาตรฐานยกเว้นปริมาณไอออนของแคลเซียม ซึ่งน่าจะเกิดจากการชะละลายของแคลเซียมจากโดโลไมต์ที่ใช้เป็นตัวเร่งปฏิกิริยา อย่างไรก็ดี เราสามารถกำจัดแคลเซียมไอออนได้ด้วยการผ่านเรซินแลกเปลี่ยนไอออนประจุบวก

ตารางที่ 6 Some fuel properties of biodiesel produced from PKO



Properties	Standard of diesel fuel	Standard of biodiesel	Biodiesel from PKO	Method
Methyl ester content (wt.%)	–	> 96.5	98.0	EN 14103
Kinematic viscosity (cSt)	1.8-4.1	3.5-5	2.82	ASTM D 445
Specific gravity at 15.6/15.6 °C	0.81-0.87	0.86-0.90	0.87	ASTM D 1298
Cetane index	> 47	> 51	52.4	ASTM D 613
Flash point (°C)	> 52	> 120	130	ASTM D 93
Heating value (MJ kg^{-1})	–	–	38.5	ASTM D 2015
Metal content (mg kg^{-1})[a]				
Group I (Na + K)	–	< 5	0.0	XRF
Group II (Ca + Mg)	–	< 5	110[b]	XRF

[a] Biodiesel product prior to washing with water.

[b] Mainly calcium ion.

2. โลหะออกไซด์ผสมสามองค์ประกอบ (Three-component mixed oxides)

2.1 การสังเคราะห์โลหะออกไซด์ผสมสามองค์ประกอบด้วยวิธีการตกตะกอนร่วม (co-precipitation)

ในการเตรียมโลหะออกไซด์ผสมสามองค์ประกอบใช้โลหะประจุบวกสองและสามหลายชนิด ได้แก่ Mg, Ca, Ba, Zn และ Al โดยใช้เกลือไนเตรตของโลหะเหล่านี้เป็นตัวตั้งต้น (precursor) และใช้โซเดียมคาร์บอเนต (Na_2CO_3) หรือแอมโมเนียคาร์บอเนต ($(NH_4)_2CO_3$) เป็นสารตกตะกอน การตกตะกอนร่วมทำที่อุณหภูมิและความดันบรรยากาศ จากนั้นกวนผสมต่อไปที่อุณหภูมิ 60 องศาเซลเซียส เป็นเวลา 8 – 20 ชั่วโมง แยกตะกอนของแข็งที่ได้ออกด้วยการกรอง ล้างไอออนโลหะที่อาจเหลืออยู่ด้วยน้ำกลั่นหลายครั้ง ทำการอบที่อุณหภูมิ 100 องศาเซลเซียส ข้ามคืน ก่อนนำไปใช้ในการเร่งปฏิกิริยาทำการเผา (calcination) ที่อุณหภูมิในช่วง 600-900 องศาเซลเซียส โดยใช้เตาเผาอุณหภูมิสูง นอกจากนั้นได้ทำการศึกษาหาภาวะที่เหมาะสมในการเตรียม ได้แก่ ชนิดของโลหะ ชนิดของสารตกตะกอน อัตราส่วนโดยโมลของ CO_3^{2-}/OH^- และอุณหภูมิในการเผาตะกอน

2.2 วิเคราะห์ลักษณะสมบัติของโลหะออกไซด์ผสมสามองค์ประกอบที่สังเคราะห์ได้

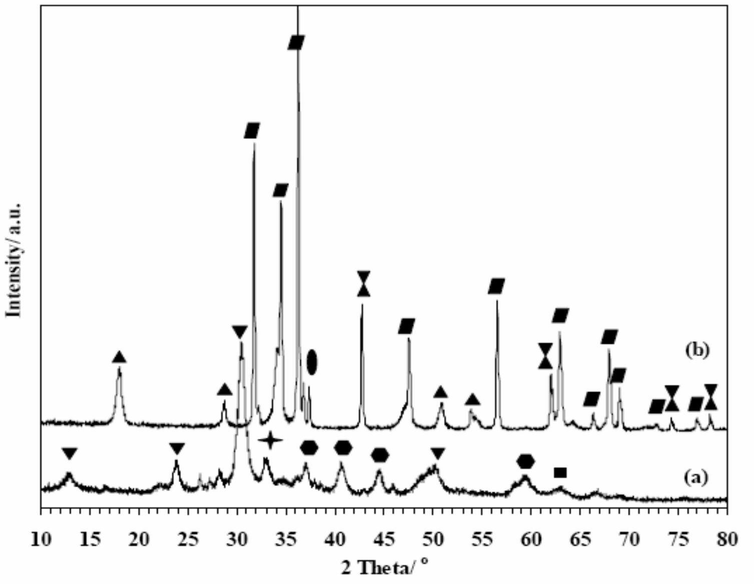
ทำเช่นเดียวกับหัวข้อ 1.2

2.3 ทดสอบความสามารถในการเร่งทรานส์เอสเทอริฟิเคชันของโลหะออกไซด์ผสมสามองค์ประกอบ

ทำเช่นเดียวกับหัวข้อ 1.3

2.4 ผลงานวิจัยที่ได้รับ

จากการทดลองปรับเปลี่ยนภาวะในการสังเคราะห์โลหะออกไซด์ผสมสามองค์ประกอบ ได้แก่ ชนิดและสัดส่วนของโลหะ ความเป็นกรด-เบสในการตกตะกอน ชนิดของสารตกตะกอน และอุณหภูมิในการเผา พบว่า ชนิดและสัดส่วนของโลหะที่ใช้ส่งผลต่อสัณฐาน ขนาดของอนุภาคและความสามารถในการเร่งทรานส์เอสเทอริฟิเคชันของโลหะออกไซด์ผสมที่เตรียมได้อย่างเห็นได้ชัด ในขณะที่ความเป็นกรด-เบสและเวลาในการบ่ม จะส่งผลต่อความสมบูรณ์ของการตกตะกอน ขนาดผลึกออกไซด์ ปริมาณของโลหะออกไซด์ผสมที่ได้ และการกระจายของโลหะแต่ละชนิดในเนื้อออกไซด์ ส่วนอุณหภูมิในการเผามีผลต่อความว่องไวของโลหะออกไซด์ที่ได้เช่นกัน ซึ่งขึ้นกับชนิดและสัดส่วนส่วนของโลหะที่เป็นองค์ประกอบ



รูปที่ 4 XRD patterns of mixed CaMgZn precipitates before (a) and after (b) the calcination at 800 ºC for 2 h.
(Symbols: ▼ = $CaZn(CO_3)_2$, ⬢ = $CaMg(CO_3)_2$, ■ = $Zn(OH)_2$, ✦ = $Mg(OH)_2$,
▲ = $Ca(OH)_2$, ⬮ = CaO, ⧗= MgO and ▰ = ZnO)

ตะกอนผสมของ Ca กับโลหะบางชนิด เช่น Mg และ Zn จะอยู่ในรูปของสารประกอบคาร์บอเนตผสม (mixed carbonate) ของแคลเซียม ได้แก่ $CaMg(CO_3)_2$ และ $CaZn(CO_3)_2$ ตามลำดับ (รูปที่ 4) เนื่องจากโครงสร้าง rhombohedral ของ $CaCO_3$ สามารถบรรจุโลหะไอออนทั้งสองชนิดนี้เข้าไปในโครงสร้างได้ โลหะอื่นๆ ที่สามารถเกิดได้ในลักษณะเดียวกันนี้ คือ Ba ปริมาณของสารประกอบโลหะคาร์บอเนตผสมจะมากหรือน้อยขึ้นกับปริมาณของไอออนคาร์บอเนตในระบบ ซึ่งจะแปรตามความเข้มข้นของสารละลายของสารตกตะกอน อัตราส่วนโมลของ CO_3^{2-}/metal ions และความเป็นกรด-เบสในการตกตะกอน (หรือปริมาณของไฮดรอกไซด์ไอออน) กรณีที่ไอออนคาร์บอเนตไม่เพียงพอ โลหะไอออนจะตกตะกอนในรูปของโลหะไฮดรอกไซด์ หลังการเผาที่อุณหภูมิมากกว่า 750 ºC คาร์บอเนตจะสลายตัวและได้ออกไซด์ของโลหะที่เกี่ยวข้อง

ตารางที่ 7 องค์ประกอบธาตุและสมบัติทางกายภาพและเคมีของโลหะออกไซด์ผสมสามองค์ประกอบของแคลเซียม

Elemental composition and physicochemical properties of Ca-based three-component oxides

Catalyst (CaM_1M_2)	Na content[a] (wt.%)	Metal atomic ratio ($Ca:M_1:M_2$)			Particle size[d] (µm)	CaO cluster size[e] (nm)	S_{BET}[f] ($m^2\ g^{-1}$)	ME content[g] (wt.%)
		Before the reaction		After the reaction				
		Mixture[b]	Precipitate[c]					
CaMgBa	1.68	1:1:1	8:1:6	10:1:7	2.1-7.6	42.8	6.7	32.2
CaMgZn	0.00		2:1:3	2:1:3	0.2-0.5	22.7	9.2	96.4
CaMgAl	16.90		3:1:2	2:1:2	*n.d.*	38.9	10.3	40.5
CaBaZn	0.00		1:1:1	1:1:2	0.8-11.7	40.8	4.9	98.8
CaBaAl	3.65		1:2:1	1:2:1	*n.d.*	46.7	7.7	67.8
CaZnAl	0.00		1:2:1	*n.d.*[h]	0.2-0.8	30.4	11.4	12.0

[a] Na content in the precipitate determined by XRF spectroscopy.

[b] Atomic ratio of metals in the synthesis mixture.

[c] Atomic ratio of metals in the precipitate determined by XRF spectroscopy.

[d] Determined by SEM technique.

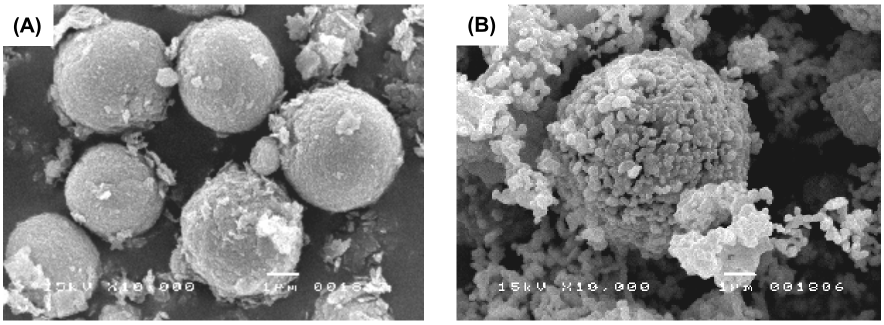
[e] Determined from XRD patterns using Sherrer's equation.

[f] BET surface area.

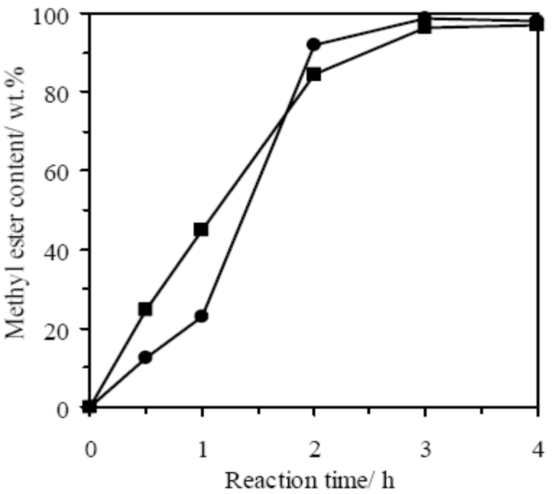
[g] Reaction conditions: methanol/oil molar ratio, 30; catalyst amount, 6 wt.%; reaction time, 3 h; temperature, 60 °C.

[h] Not determined.

ตารางที่ 7 แสดงผลการวิเคราะห์ลักษณะสมบัติและการเร่งทรานส์เอสเทอริฟิเคชันของโลหะออกไซด์ผสมสามองค์ประกอบที่สังเคราะห์ได้ โลหะออกไซด์ผสมสามองค์ประกอบมีพื้นที่ผิวน้อยเนื่องจากโครงสร้างไม่มีรูพรุน และมีลักษณะการจับรวมกันเป็นกลุ่มก้อน (รูปที่ 5) การทดสอบการเร่งปฏิกิริยาทรานส์เอสเทอริฟิเคชันที่อัตราส่วนโดยโมลของเมทานอลต่อน้ำมันเท่ากับ 30 ปริมาณตัวเร่งปฏิกิริยา 10% เทียบกับน้ำหนักน้ำมัน อุณหภูมิ 60 องศาเซลเซียส และเวลา 3 ชั่วโมง พบว่า ออกไซด์ผสมสามองค์ประกอบของ CaMgZn และ CaBaZn ให้ผลได้ของเมทิลเอสเทอร์มากกว่า 95% โดยที่ CaMgZn เร่งปฏิกิริยาได้เร็วกว่า (รูปที่ 6) ผลได้ของผลิตภัณฑ์เอสเทอร์ที่ได้จากการใช้ CaBaAl เป็นตัวเร่งปฏิกิริยาคือ 68% ขณะที่ CaMgBa, CaMgAl และ CaZnAl เร่งปฏิกิริยาได้ช้ากว่ามาก งานวิจัยในส่วนนี้ไม่พบความสัมพันธ์ของพื้นที่ผิวจำเพาะและขนาดอนุภาคกับความสามารถในการเร่งทรานส์เอสเทอริฟิเคชัน ความว่องไวในการเร่งปฏิกิริยาจะเพิ่มขึ้นเมื่อปริมาณของแคลเซียมมากขึ้น นอกจากนั้นพบว่า โลหะออกไซด์ผสมสามองค์ประกอบบางชนิดมีสัดส่วนของโลหะเปลี่ยนแปลงไปหลังการใช้ในปฏิกิริยา แสดงว่าเกิดการละลายของโลหะบางส่วนในเมทานอล

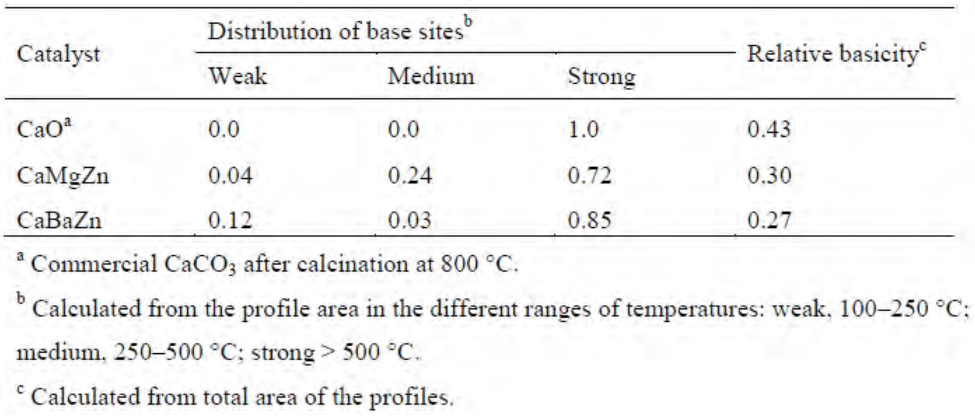


รูปที่ 5 SEM images of CaMgZn precipitates (A) before and (B) after calcination at 800 ºC.



รูปที่ 6 Dependence of the ME content on time in the transesterification of PKO with methanol over CaMgZn (■) and CaBaZn (●). Reaction conditions: methanol/oil molar ratio, 30; catalyst amount, 6 wt.%; temperature, 60 °C.

ตารางที่ 8 Relative basicity of various mixed oxides determined by temperature-programmed desorption (TPD) of CO_2



Catalyst	Distribution of base sites[b]			Relative basicity[c]
	Weak	Medium	Strong	
CaO[a]	0.0	0.0	1.0	0.43
CaMgZn	0.04	0.24	0.72	0.30
CaBaZn	0.12	0.03	0.85	0.27

[a] Commercial $CaCO_3$ after calcination at 800 °C.

[b] Calculated from the profile area in the different ranges of temperatures: weak, 100–250 °C; medium, 250–500 °C; strong > 500 °C.

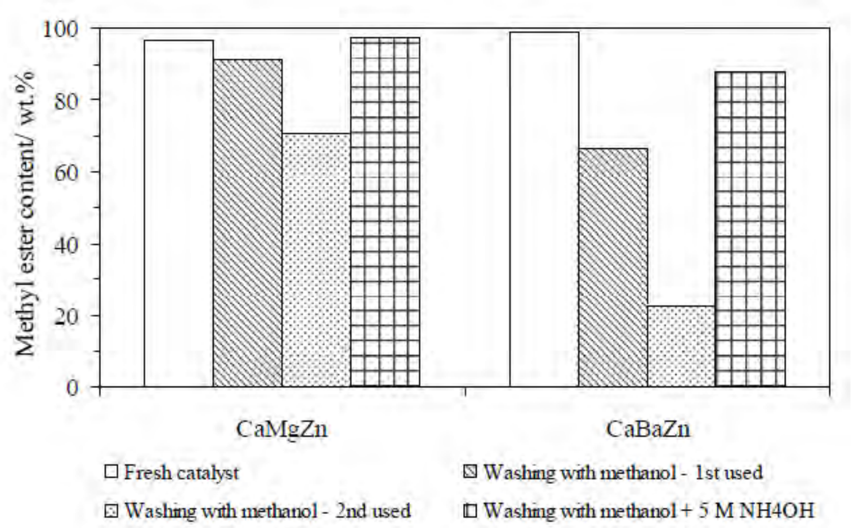
[c] Calculated from total area of the profiles.

ผลการวิเคราะห์สมบัติความเป็นเบส (basic properties) ด้วยเทคนิค TPD ของ CO_2 ของออกไซด์ผสม CaMgZn และ CaBaZn แสดงในตารางที่ 8 โลหะออกไซด์ผสมทั้งสองชนิดประกอบด้วยตำแหน่งเบสที่มีความแรงเบสแรง (strong base sites) เป็นหลัก แต่ CaMgZn จะมีตำแหน่งเบสที่ความแรงเบสปานกลาง (medium base sites) มากกว่า CaBaZn อย่างเห็นได้ชัด ซึ่งส่งผลให้ปริมาณตำแหน่งเบสรวมของ CaMgZn มากกว่า CaBaZn ด้วยเหตุผลนี้น่าจะทำให้อัตราเร็วในการเร่งปฏิกิริยาทรานส์เอสเทอริฟิเคชันด้วย CaMgZn สูงกว่า CaBaZn (รูปที่ 6)

รูปที่ 7 แสดงผลของการฟื้นฟูสภาพตัวเร่งปฏิกิริยา CaMgZn เปรียบเทียบกับ CaBaZn ซึ่งในการศึกษานี้ใช้วิธีการล้าง (washing method) เป็นหลัก เนื่องจากเป็นวิธีการที่ประหยัดพลังงานและสารละลายที่ใช้ในการล้างสามารถนำมาใช้ได้หลายครั้ง ในกรณีการล้างด้วยเมทานอลพบว่า เมทิลเอสเทอร์ที่ได้จะลดลงเรื่อยๆ โดย CaMgZn จะยังคงให้ผลได้ของเมทิลเอสเทอร์สูงกว่า CaBaZn การล้าง

ด้วยสารละลายเมทานอลผสม NH_4OH ความเข้มข้น 5 โมลาร์ ทำให้การเร่งปฏิกิริยาของโลหะออกไซด์ผสมทั้งสองชนิดกลับมาสูงขึ้นอีกครั้ง งานวิจัยก่อนหน้านี้แสดงให้เห็นว่ากลีเซอรอลที่เป็นผลิตภัณฑ์ข้างเคียงสามารถทำปฏิกิริยากับ CaO และเกิดเป็นแคลเซียมกลีเซอรอไซด์ (calcium glyceroxide, $Ca(O_3H_7C_3)_2$) ซึ่งจะปกคลุมผิวหน้าของตัวเร่งปฏิกิริยาไว้ทำให้ปฏิกิริยาเกิดได้น้อยลง การล้างด้วยตัวทำละลายที่มีน้ำเป็นองค์ประกอบ (5M NH_4OH) จะทำให้เกิดไฮโดรไลซิสและได้ CaO กลับมาดังสมการ

$$Ca(O_3H_7O_3)_{2(s)} + H_2O_{(l)} \longleftrightarrow CaO_{(s)} + 2C_3H_8O_{3(l)}$$



รูปที่ 7 Effects of regeneration method on transesterification of PKO with methanol over CaMgZn and CaBaZn. Reaction conditions: methanol/oil molar ratio, 30; catalyst amount, 6 wt.%; temperature, 60 °C.

ข้อเสนอแนะในการทำวิจัยต่อไป

แม้ว่าตัวเร่งปฏิกิริยาออกไซด์ผสมของ Ca กับ Mg, Ba และ Zn จะเร่งทรานส์เอสเทอริฟิเคชันของน้ำมันพืชกับเมทานอลได้อย่างว่องไวและให้ผลได้ของเมทิลเอสเทอร์สูง แต่ตัวเร่งปฏิกิริยาชนิดนี้ยังคงประสบปัญหาการชะละลายขององค์ประกอบที่ว่องไว ทำให้มีข้อจำกัดในการนำกลับมาใช้ใหม่ (reusablity) ดังนั้นงานวิจัยในขั้นต่อไป ควรศึกษาผลของโครงสร้างของตัวเร่งปฏิกิริยาที่มีต่อการชะละลายขององค์ประกอบที่ว่องไวและการนำกลับมาใช้ใหม่

Output จากโครงการวิจัยที่ได้รับทุนจาก สกว.

1. ผลงานตีพิมพ์ในวารสารวิชาการระดับนานาชาติ

2. การนำเสนอผงานในที่ประชุมวิชาการระดับนานาชาติ

ภาคผนวก

Manuscript ที่ส่งตีพิมพ์ไปแล้วในช่วง 16 มีนาคม 2552 – 15 มีนาคม 2553 จำนวน 2 เรื่อง

1) C. Ngamcharussrivichai, P. Nunthasati, S. Tanachai "Biodiesel production through transesterification over natural calciums" *Fuel Processing Technology*.
2) C. Ngamcharussrivichai, P. Totarat, S. Limmanee, W. Meechan, K. Bunyakiat "Ca-based three-component mixed oxides as heterogeneous base catalysts for methanolysis of palm kernel oil" *Catalysis Today*.

การนำเสนอผลงานในการประชุมวิชาการระดับนานาชาติ ในช่วง 16 มีนาคม 2552 – 15 มีนาคม 2553 จำนวน 1 เรื่อง

S. Limmanee, P. Totarat, W. Meechan, C. Ngamcharussrivichai "Ca-based three-component mixed oxides as heterogeneous base catalysts for methanolysis of palm kernel oil" *Abstract Book of The 7th Asia Pacific Conference on Sustainable Energy and Environmental Technology (APCSEET 2009)*, 15-17 October 2009, Qingda

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Biodiesel production through transesterification over natural calciums

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ABSTRACT

Transesterification of palm kernel oil (PKO) with methanol over various natural calciums, including limestone calcite, cuttlebone, dolomite, hydroxyapatite, and dicalcium phosphate, has been investigated at 60 °C and 1 atm. The study showed that dolomite, mainly consisting of $CaCO_3$ and $MgCO_3$, is the most active catalyst. The calcination temperature largely affected the physicochemical properties, as evidenced by N_2 adsorption–desorption measurement, TGA, SEM and XRD, and the transesterification performance of the resultant catalysts. It was found that the calcination of dolomite at 800 °C resulted in a highly active mixed oxide. CaO was suggested to be the catalytically active site responsible for the methyl ester formation. Under the suitable reaction conditions, the amount of dolomite calcined at 800 °C = 6 wt.% based on the weight of oil, the methanol/oil molar ratio = 30, and the reaction time = 3 h, the methyl ester content of 98.0% can be achieved. The calcined dolomite can be reused many times. The analyses of some important fuel properties indicated that the biodiesel produced had the properties that meet the standard of biodiesel and diesel fuel issued by the Department of Energy Business, Ministry of Energy, Thailand.

1. Introduction

Due to the current energy situation and environmental constrains, search for green and renewable fuels has been made worldwide. Vegetable oils and animal fats are biomass-based candidate sources for the clean fuel production due to their non-toxicity, biodegradability, and zero sulfur and aromatic content [1]. However, a direct use of oils and fats as fuels in modern high-speed engines is prohibited because their physicochemical properties are largely different from the standard hydrocarbon fuels. Transesterification or alcoholysis is an effective route to convert high viscosity triglycerides, the major components in oils and fats, to less viscous mono-alkyl esters, so-called biodiesel, by reacting with small alcohols, such as methanol. The physicochemical and fuel properties of biodiesel are categorized into the same range of petroleum diesel. Thus, it can be applied to compression–ignition diesel engines with little or no modifications.

The current technologies for biodiesel production are based on homogeneously catalyzed transesterification under basic [2–5] or acidic [6–8] conditions. Although the reaction is easily performed at low temperatures, the subsequent separation and purification steps are time-consuming and non-environmentally friendly due to a requirement of several washing stages. Consequently, a considerable amount of highly caustic wastewater is inevitably produced. These drawbacks significantly contribute some additional cost to the final product. To overcome these problems, more environmentally benign routes to the methyl esters have been extensively researched and developed [9–23]. Using heterogeneous catalysts has received much attention since the reaction proceeds under relatively mild conditions at an acceptable rate and the process can be simplified by facilitating the separation and purification, and omitting the washing stage [9].

Natural $CaCO_3$ rock has low activity, and a high reaction temperature (>200 °C) was required to achieve the oil conversion of >95% [17]. Although Al_2O_3-supported alkali metal oxide catalysts are more basic and very active [10–13], their active phases are highly sensitive to moisture and easily leached by methanol [24]. CaO is a solid base catalyst widely investigated in the transesterification [16,18–23]. Despite its low cost and availability, CaO with high basic strength ($H\_ = 26.5$) possesses high activity and long service lifetime [23]. Commercially, CaO is produced via a thermal decomposition of limestone calcite at high temperatures [25]. Other $CaCO_3$-based materials, including coral, sea shells, and chalk, can be also used as the sources of CaO.

Dolomite is a naturally abundant carbonate rock found in several areas of Thailand. At present, the major domestic usage of dolomite is cement manufacturing and landfill due to its very low cost. While calcite is defined as high purity $CaCO_3$, dolomite consists of $CaCO_3$ and $MgCO_3$ with a small amount of ferrite and silica. Similarly to calcite, upon a simple calcination of dolomite at high temperatures, the carbonate groups are decomposed, generating the base oxides. To our best knowledge, dolomite has received, however, much less attention as a base catalyst regardless of its high basicity, low cost, less toxicity,

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and environmental friendliness. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) and dicalcium phosphate ($CaHPO_4$) are also natural calcium compounds. Their catalytic activity in the base-catalyzed reactions was reported in literature [26,27].

In the present study, we have investigated the possibility to use various types of natural calciums as the catalysts for the methanolysis of palm kernel oil, which is readily available at relatively low price in Thailand. The calcium materials applied to the study included calcite, cuttlebone, dolomite, hydroxyapatite and dicalcium phosphate. The effects of calcination temperatures on the physicochemical properties of the resultant catalysts as well as the effects of reaction conditions on the formation of methyl esters have been investigated.

2. Experimental section

2.1. Catalyst preparation

Calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) were obtained from Thai Dolomite Co., Ltd. located in Surat Thani Province, Thailand. Cuttlebone was scraped from splendid squid (*Loligo formosana* Sasaki). It is one of the most abundant species in the Gulf of Thailand. Elemental composition analysis with XRF spectroscopy indicated that calcite and cuttlebone consist of $CaCO_3 > 91$ wt.%, while dolomite is composed of CaO 16.56%, MgO 31.20%, Fe_2O_3 298 ppm, SrO 198 ppm and CO_2 balance. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) and dicalcium phosphate ($CaHPO_4$) were analytical reagent (AR grade) from Ajax Finechem, and used without further purification. Before being used as a catalyst, the calcium compounds were ground and sieved to <10 μm, followed by calcination in a muffle furnace at 600–900 °C for 2 h.

2.2. Catalyst characterization

Crystalline structures of natural calciums applied to the study were confirmed by a technique of powder X-ray diffraction (XRD) using a Rigaku DMAX 2200/Ultima+ diffractometer equipped with Cu Kα radiation. Elemental analysis was performed on a JEOL ED-2000 energy dispersive X-ray fluorescence (XRF) spectrometer. Morphology of calcined dolomites was analyzed with a JEOL JSM-5800LV scanning electron microscope (SEM). Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer Pyris Diamond thermogravimetry (TG/DTA) with a temperature ramp rate of 8 °C min^{-1} under dry air flow. BET surface area, average pore size and average pore volume were measured by a N_2 adsorption–desorption technique using a Micromeritic ASAP 2020 surface area and porosity analyzer.

2.3. Transesterification procedure

Refined bleached deodorized palm kernel oil (PKO) was donated by Chumporn Palm Oil Industry Co., Ltd. Its fatty acid composition and physicochemical properties are illustrated in Tables 1 and 2, respectively. The transesterification was carried out in a 250-mL 3-neck round bottom flask equipped with a condenser and a magnetic stirrer. Typically, a calcined catalyst was suspended in a required volume of methanol (99.5%, commercial grade). Temperature of the slurry was controlled at 60 °C by a water bath. Subsequently, the oil was added under vigorous stirring. The methanol/oil molar ratio was varied between 15 and 70. After the course of reaction, the catalyst was separated by centrifuge, and the reaction mixture was then loaded into a rotary evaporator to remove excess methanol. The remaining product was washed with deionized water, and the upper layer was recovered and dried with anhydrous Na_2SO_4. Composition of methyl esters was analyzed with a Shimadzu 14B gas chromatograph (GC) equipped with a FID detector and a 30-m DB-Wax capillary column. The amount of the methyl esters produced was calculated based on the standard method EN 14103 using methyl heptadecanoate as the reference standard. Methyl ester (ME) content, equivalent to the methyl ester yield, is defined as follows:

$$\text{ME content (wt.\%)} = \frac{\text{Weight of methyl esters calculated by GC}}{\text{Weight of methyl ester phase}} \times 100. \tag{1}$$

When a quantitative analysis of remaining was required, a Varian CP-3800 gas chromatograph equipped with a FID detector and a 15-m DB-1ht capillary column was used. The analysis was performed according to the standard method of EN 14105.

Table 1
Fatty acid composition of palm kernel oil used in the present study.

Fatty acid	Composition (wt.%)
C 6:0 Caproic acid	0.24
C 8:0 Capryric acid	5.14
C 10:0 Capric acid	4.82
C 12:0 Lauric acid	59.83
C 14:0 Myristic acid	14.92
C 16:0 Palmitic acid	5.38
C 18:0 Stearic acid	1.52
Saturated	*91.85*
C 18:1 Oleic acid	6.87
C 18:2 Linoleic acid	1.28
Unsaturated	*8.15*
Total fatty acid	100
Average molecular weight	677

Table 2
Physicochemical properties of palm kernel oil used in the present study.

Properties	Analysis results
Density at 15 °C (g mL^{-1})	0.922
Kinematic viscosity at 40 °C (mm^2 s^{-1})	28.52
Acid number (mg_{KOH} $g^{-1}{}_{oil}$)	0.14
Moisture content (wt.%)	0.1
Iodine value (g_{I2} $kg^{-1}{}_{oil}$)	1.755

3. Results and discussion

3.1. Screening types of natural calciums

Table 3 shows the ME content in the biodiesel product obtained over various natural calciums calcined at 800 °C for 2 h. The data for CaO, $MgCO_3$ and MgO were compared. Calcite gave a moderate ME content (46.8%). This result is in accordance with the previous work by Suppes et al. [17]. $CaCO_3$-based cuttlebone also catalyzed the transesterification of PKO but to a lesser extent. Interestingly, the ME content as high as 98.6% was attained over the calcined dolomite with mixed alkali earth metals. It is worth noting that the activity of the calcined dolomite is relatively high when compared to other heterogeneous catalysts reported earlier [28]. Peterson and Scarrah

Table 3
Methyl ester content in the biodiesel produced via transesterification[a] of PKO over various natural calciums calcined at 800 °C.

Catalyst	Methyl ester content (wt.%)
Calcite	46.8
Cuttlebone	24.1
Hydroxyapatite	2.6
Dicalcium phosphate	1.3
Dolomite	98.6
CaO	92.8
$MgCO_3$	1.2
MgO	0.7

[a] Reaction conditions: catalyst amount, 6 wt.%; methanol/oil ratio, 30; temperature, 60 °C; time, 3 h.

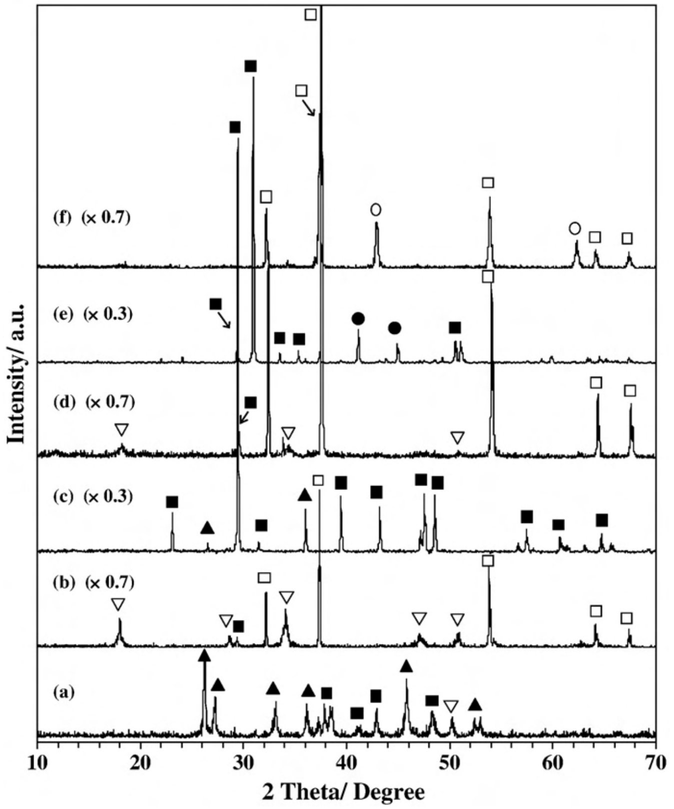


Fig. 1. XRD patterns of non-calcined cuttlebone (a), cuttlebone calcined at 800 °C, 2 h (b), non-calcined calcite (c), calcite calcined at 800 °C, 2 h (d), non-calcined dolomite (e), and dolomite calcined at 800 °C, 2 h (f). (Symbols: ▲ = aragonite $CaCO_3$, ■ = calcite $CaCO_3$, ● = $MgCO_3$, □ = CaO, ○ = MgO and ▽ = $Ca(OH)_2$).

observed a remarkable improvement of CaO activity by the impregnation of Ca on MgO support [18]. This result suggested the presence of synergetic effect between two different metals in a bifunctional catalysis route. On the other hand, trace amount of methyl esters was attained when the reaction was catalyzed by hydroxyapatite and dicalcium phosphate. Indeed, the phosphate group itself possesses some acidity. Upon a high temperature calcination, $Ca_{10}(PO_4)_6(OH)_2$ with apatite structure and $CaHPO_4$ with brushite structure can be converted to other forms of phosphate compounds, for example calcium pyrophosphate ($Ca_2P_2O_7$) [29], which is much less basic than CaO. Therefore, the calcined calcium phosphates may not provide a sufficient basicity for the transesterification of triglycerides.

Similarly to the results in literature [16,18–23], CaO is a good catalyst for transesterification of PKO. A high temperature calcination of $CaCO_3$-based materials also gives the basic CaO sites. It was reported that the decomposition of $CaCO_3$ as a limestone to generate the CaO phase usually occurs at temperatures higher than 800 °C, preferentially at 825–900 °C under atmospheric pressure [25]. It is likely that the difference in the ME content attained over calcite, cuttlebone and dolomite was related to the extent of decarbonation of each material after the calcination at 800 °C for 2 h.

It was clearly indicated by the XRD patterns that, before the calcination, cuttlebone had a different crystal structure to calcite and dolomite (Fig. 1). The former was mainly present in the form of orthorhombic aragonite $CaCO_3$ (Fig. 1a), while the latter carbonates possessed a rhombohedral structure (Fig. 1c and e, respectively). After the calcination at 800 °C, most of diffraction peaks related to carbonates disappeared concomitantly with the presence of intense peaks of cubic CaO (Fig. 1b, d and f). However, the detailed XRD analysis using JCPDS files indicated that $CaCO_3$ ($2\theta = 29.4°$) remained in cuttlebone and calcite (Fig. 1b and d, respectively). This result suggested the higher extent of decarbonation of dolomite when compared to cuttlebone and calcite. The presence of both Ca and Mg could promote the decarbonation of dolomite to the corresponding oxides. Moreover, $Ca(OH)_2$ phase, formed by the hydration of CaO, appeared on the calcined cuttlebone (Fig. 1b) and calcite (Fig. 1d). The formation of $Ca(OH)_2$ occurred readily upon an exposure of CaO to ambient air, resulting in a significant loss of the transesterification activity [22]. The absence of $Ca(OH)_2$ in the calcined dolomite is unclear although all catalysts were treated under the same environment. Perhaps, it is related to the crystalline structure and the elemental composition of the materials themselves.

It was reported that MgO and CaO can be generated from the calcination of dolomite at temperatures lower than 800 °C, when compared to that of calcite and aragonite $CaCO_3$ (>800 °C for a complete decarbonation) [25]. The calcination of dolomitic rock with high calcite content requires the temperatures >900 °C [30]. From the TGA experiment (Fig. 2), dolomite exhibited the major weight loss at 754 °C, corresponding to 47.5 wt.% (the theoretical weight loss = 52.5 wt.%), whereas calcite had a large weight loss at higher temperature, suggesting that dolomite was decarbonated more easily than calcite. The small difference of the temperature (32 °C) may be due to the presence of dry air flow that facilitates removal of CO_2 from the particle surface. The decarbonation is a reversible reaction, which greatly depends on CO_2 concentration in atmosphere, partial pressure, and elemental composition and particle size of carbonate compound [25]. The dissociation of CO_2 always proceeds gradually from the outside surface inward. A formation of CO_2 film on the external surface is expected to occur when the dissociation inside the particle is in progress, leading to the recarbonation of CaO to $CaCO_3$. Therefore, the calcination temperature required for the complete decomposition of the carbonate groups in a muffle furnace should be higher than that observed from the TG analysis. In addition, the prolongation of calcination time for both calcite and dolomite from 2 h to 4 and 6 h did

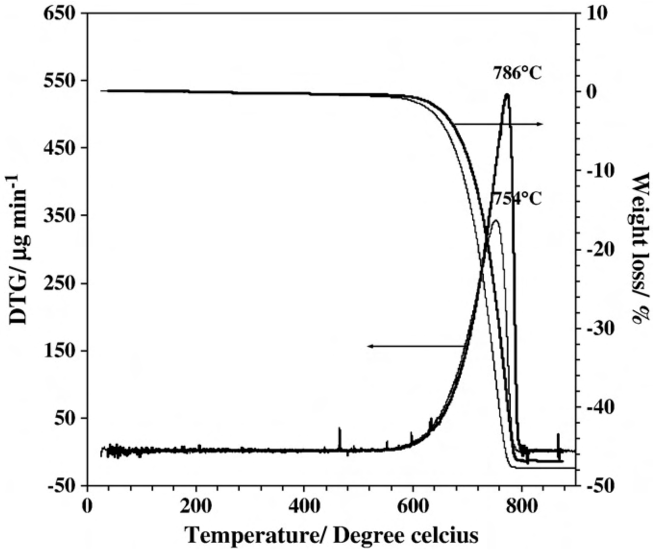


Fig. 2. Weight loss and DTG curves for calcite (thick line) and dolomite (thin line).

Table 4
Methyl ester content in the biodiesel produced via transesterification[a] of PKO over dolomite calcined at various temperatures.

Calcination temperature (°C)	Methyl ester content (wt.%)
600	0.0
700	0.0
800	98.6
900	81.2

[a] Reaction conditions: catalyst amount, 6 wt.%; methanol/oil ratio, 30; temperature, 60 °C; time, 3 h.

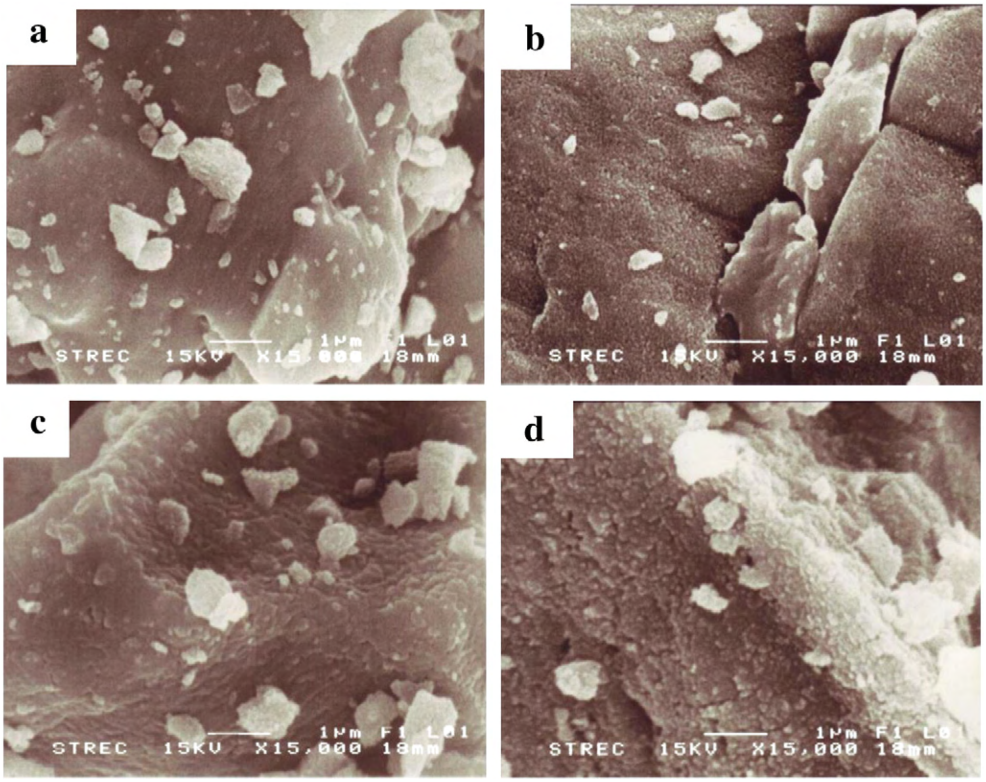


Fig. 3. SEM images for dolomite calcined at 600 (a), 700 (b), 800 (c) and 900 °C (d).

not alter the ME content significantly. This result was consistent with the work by Ray and Mathers who reported that the increase in the temperature exerts a much greater influence on the CO_2 dissociation rate than the temperature retention [31].

From the screening results, the calcined dolomite is the best catalyst for the transesterification of PKO. Hereafter, the effects of the calcination temperatures of dolomite on the catalytic performance of the resulting mixed oxides were studied, and the suitable conditions for the transesterification over the calcined dolomite were investigated.

3.2. Effect of calcination temperature of dolomite

Dolomites calcined at 600 and 700 °C for 2 h did not catalyze the transesterification (Table 4). The ME content of 98.6% was achieved when the calcination was performed at 800 °C. However, further increasing the temperature to 900 °C decreased the ME content to 81.2%. These results should be related to the extent of decarbonation of dolomite at different calcination temperatures, providing the different amounts of active basic sites for the transesterification.

The SEM images of dolomites calcined at different temperatures revealed an increase in the roughness of dolomite surface with the calcination temperature (Fig. 3). The presence of the roughness was noticeable at the temperature of >700 °C (Fig. 3b). It should be derived from the decomposition of the carbonate groups, liberating CO_2 concomitantly with the formation of small pores. The N_2 adsorption–desorption measurement indicated an increase in the BET surface area and the average pore volume with the calcination temperature (Table 5). The maximum surface area of 19.58 $m^2\,g^{-1}$ was observed when dolomite was calcined at 800 °C, while at the lower temperatures the surface area was slightly changed. This result suggested that the decomposition of carbonates is accomplished at 800 °C. It should be noted that, at the calcination temperature of 900 °C, there were large fractures appearing on the surface (Fig. 3d). These should be due to a severe reduction of unit cell after the

Table 5
Textural properties of dolomite calcined at different temperatures.

Calcination temperature (°C)	S_{BET}[a] ($m^2\,g^{-1}$)	V_p[b] ($cm^3\,g^{-1}$)	D_p[c] (Å)
Before calcination	0.45	0.002	181.9
600	0.80	0.008	222.1
700	1.87	0.009	202.2
800	19.58	0.106	214.8
900	19.04	0.063	145.4

[a] BET surface area.
[b] Average pore volume.
[c] Average pore diameter.

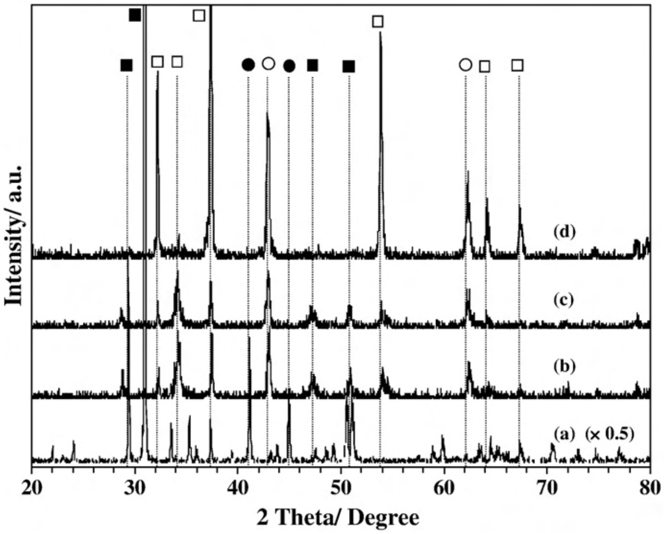


Fig. 4. XRD patterns of non-calcined dolomite (a) and dolomites calcined at 600 (b), 700 (c) and 800 °C (d). (Symbols: ■ = calcite $CaCO_3$, ● = $MgCO_3$, □ = CaO and ○ = MgO).

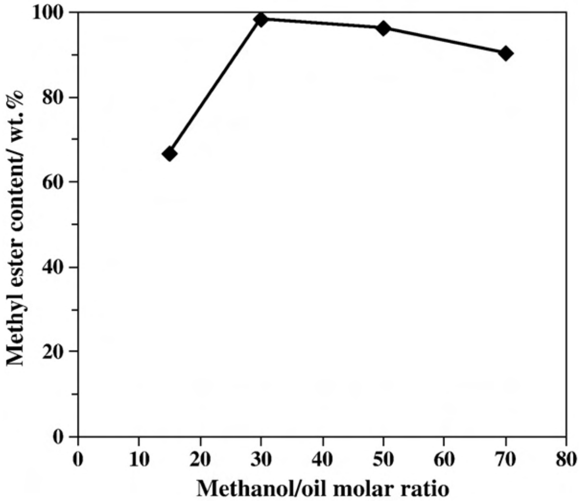


Fig. 5. Dependence of methyl ester content on methanol/oil molar ratio over dolomite calcined at 800 °C. Reaction conditions: catalyst amount, 6 wt.%; time, 3 h; temperature, 60 °C.

complete decarbonation [25]. The surface fraction was reflected by a significant decrease in the average pore volume and pore size (Table 5). Boynton reported the sintering effect related to the calcination of limestones at high temperatures, which results in a dense and unreactive lime [25].

The XRD patterns of dolomites calcined at different temperatures are shown in Fig. 4. The major phases existing in the parent dolomite were $CaCO_3$ and $MgCO_3$ (Fig. 4a). The calcination at 600 and 700 °C (Fig. 4b and c, respectively) was sufficient to decompose $MgCO_3$, yielding MgO, but did not preferentially decompose $CaCO_3$. A large amount of CaO phase was generated when the calcination was performed at 800 °C. These results are consistent with the results obtained from TGA (Fig. 2).

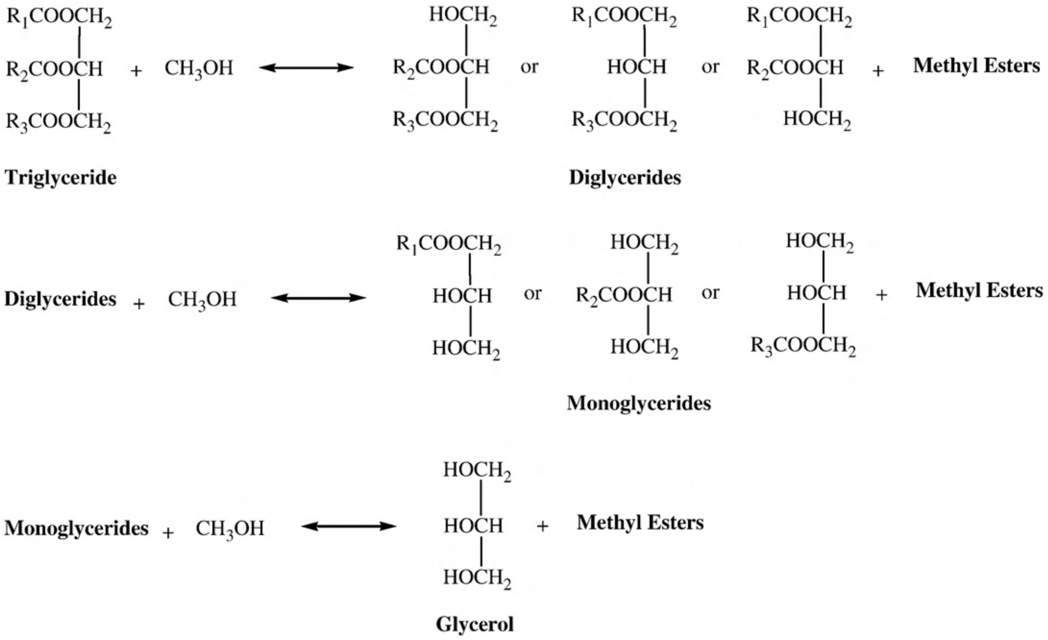
The decarbonation of $MgCO_3$ at the lower temperatures suggested the relatively weak basic character of MgO, compared to CaO. It was shown by the temperature-programmed desorption (TPD) of CO_2 that CaO possesses both the basic strength and density higher than MgO [32]. Therefore, the basic sites responsible for the transesterification over the calcined dolomite were mainly CaO derived from $CaCO_3$ that requires the decomposition temperature higher than 725 °C (Fig. 2). MgO formerly generated may be sintered and dense, resulting in a lower reactivity [25]. Based on the present results, it is clear that the calcination at 800 °C produces an efficient solid base for the transesterification of PKO.

3.3. Effect of methanol/oil molar ratio

Fig. 5 reveals the effect of methanol/oil molar ratios on the transesterification of PKO over dolomite calcined at 800 °C. Under the studied conditions, there was no soap formed in all experiments. With increasing the ratio from 15 to 30, the ME content increased from 66.5 to 98.6%. However, a drop of the ME content was seen after the methanol/oil molar ratio was further increased to 50 and 70. Since the transesterification is reversible in nature, this result may be due to the reverse reaction between glycerol and methyl esters produced to form the triglyceride derivatives, i.e. monoglycerides and diglycerides (Scheme 1), reducing the yield of methyl esters. The occurrence of reverse reaction was supported by the fact that we observed a homogeneous liquid phase after the course of reaction and the gravitational separation between the methyl ester and glycerol layers was very difficult when the reaction was carried out at the high ratios. Monoglycerides and diglycerides can behave molecularly like a co-solvent, and homogenize the phases of methanol, glycerol and methyl esters [33]. From the present results, the suitable methanol/oil molar ratio for the transesterification of PKO over dolomite calcined at 800 °C is, therefore, 30.

3.4. Effect of reaction time

The change of product distribution on time in the transesterification of PKO over dolomite calcined at 800 °C is shown in Fig. 6. The triglyceride conversion of 30% was attained within 30 min. The absence of induction period at the early stage of the reaction should be ascribed to the fact that the calcined dolomite possessed the large pore sizes (Table 5), probably as the interparticle voids. The maximum ME yield of 98.6% was achieved when the reaction was carried out for 3 h. The detected amount of monoglycerides was low because its



Scheme 1. Transesterification of representative triglyceride to methyl esters and diglycerides, monoglycerides and glycerol, respectively.

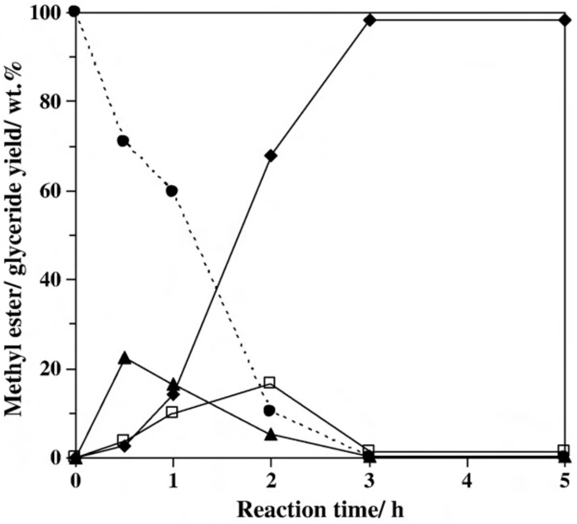


Fig. 6. Dependence of methyl ester content on reaction time over dolomite calcined at 800 °C. Reaction conditions: methanol/oil molar ratio, 30; catalyst amount, 6 wt.%; temperature, 60 °C. (Symbols: ● = triglycerides, ▲ = diglycerides, □ = monoglycerides and ♦ = methyl esters).

transformation to methyl esters proceeded at a high rate. The remaining monoglycerides were not methanolyzed although the reaction was continued up to 5 h. The results here indicated that the suitable reaction time required for achieving the highest amount of methyl esters is 3 h.

3.5. Effect of catalyst amount

It was revealed in Fig. 7 that the ME content proportionally increased with increasing the amount of calcined dolomite. This result implied that the increase in the methyl ester formation was due to the increase in the number of active basic sites. The comparative study of various solid base catalysts in the transesterification of soybean oil and the isomerization of 1-butene suggested that the activity of catalyst in the transesterification is closely related to the amount of basic sites, but not directly related to the basic strength [11]. When the amount of calcined dolomite was increased to 6 wt.%, the ME content was not altered. From the study on the effects of reaction conditions, it can be concluded that the suitable conditions for the transesterification of PKO with methanol over the calcined dolomite are the methanol/oil molar ratio of 30, the catalyst amount of 6 wt.%, and the reaction time of 3 h at 60 °C.

3.6. Reusability of dolomite catalyst

The reusability of dolomite catalyst is also investigated. Dolomite was previously calcined at 800 °C for 2 h before being applied to the first run. After the reaction course, the catalyst was recovered by centrifuge and thoroughly washed with methanol. As shown in Fig. 8, the ME content higher than 90% was maintained within the seventh repetition. When compared to the previous work [23], the calcined dolomite can be reused in fewer repetition times than CaO. This reflects the difference in the number of the active site and the reaction conditions. Also, the regeneration procedure largely influences the performance of the catalyst in the next use [34]. Although there was a significant loss of the active site by methanol leaching (Table 6), dolomite is very cheap and abundantly available in many parts of Thailand. It is our belief that dolomite has a potential to be further developed for a large-scale production of biodiesel under heterogeneous catalysis conditions. Currently, we are developing a laboratory-scale continuous flow process for transesterification of vegetable oils using dolomite and modified dolomite [15] as the heterogeneous base catalysts.

3.7. Fuel properties of biodiesel produced

To investigate some physicochemical and fuel properties of biodiesel produced, we carried out the transesterification of PKO in a 3-L stainless steel stirred tank equipped with a 4-blade propeller and a motor. An external heater and a temperature controller were used to maintain the reaction temperature at 60 °C. Other parameters were set according to the suitable reaction conditions. Except for the viscosity, the properties of our biodiesel met the biodiesel standard issued by the Department of Energy Business, Ministry of Energy, Thailand (Table 6). The viscosity lower than the standard should be attributed to the fatty acid composition of the starting oil that mainly consists of C_{12} (Table 1). However, the viscosity of the biodiesel is categorized in the standard of diesel fuel (Table 6). The test according to ASTM D 97 indicated that the present biodiesel possessed pour point lower than the biodiesel derived from palm oil. This result suggested the use of the PKO methyl esters as an additive for adjusting the cold flow properties of the conventional biodiesel.

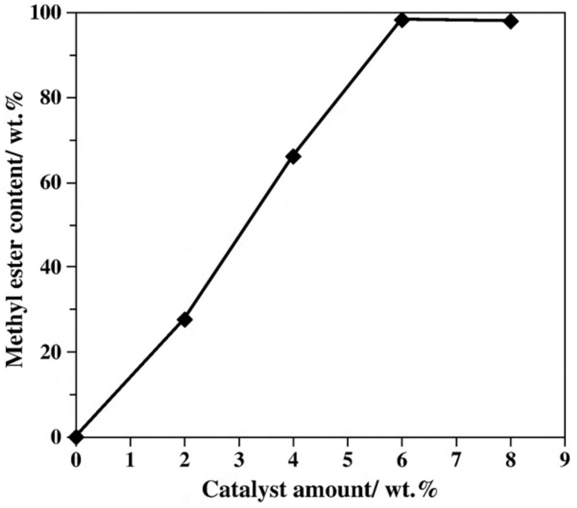


Fig. 7. Dependence of methyl ester content on amount of dolomite calcined at 800 °C. Reaction conditions: methanol/oil molar ratio, 30; time, 3 h; temperature, 60 °C.

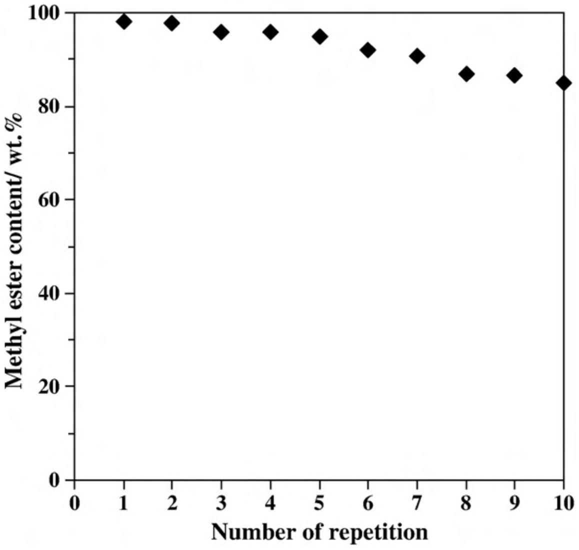


Fig. 8. Reusability test of dolomite calcined at 800 °C. Reaction conditions: methanol/oil molar ratio, 30; catalyst amount, 6 wt.%; time, 3 h; temperature, 60 °C.

Table 6
Comparison of some properties of biodiesel produced in this work with the standard of diesel fuel and biodiesel issued by the Department of Energy Business, Ministry of Energy, Thailand.

Properties	Standard of diesel fuel	Standard of biodiesel	Biodiesel from PKO	Method
Methyl ester content (wt.%)	–	>96.5	98.0	EN 14103
Kinematic viscosity (cSt)	1.8–4.1	3.5–5	2.82	ASTM D 445
Specific gravity at 15.6/15.6 °C	0.81–0.87	0.86–0.90	0.87	ASTM D 1298
Cetane index	>47	>51	52.4	ASTM D 613
Flash point (°C)	>52	>120	130	ASTM D 93
Heating value (MJ kg^{-1})	–	–	38.5	ASTM D 2015
Metal content (mg kg^{-1})[a]				
Group I (Na + K)	–	< 5	0.0	XRF
Group II (Ca + Mg)	–	< 5	110[b]	XRF

[a] Biodiesel product prior to washing with water.
[b] Mainly calcium ion.

Despite the advantages of dolomite regarding availability, cost, preparation method and environmental concerns, to our best knowledge, the achievement of the methyl ester yield of 98% over the heterogeneous catalysts at 60 °C is rare [36]. Using calcite limestone as the starting material for the preparation of CaO catalyst required the temperature as high as 1000 °C [35]. The leaching of active metal is an expectable phenomenon for CaO-based catalysts as well as other alkali earth oxides [36]. The contamination of metal cation can be simply removed by an adsorption on ion-exchange resin [35].

4. Conclusions

Our present study revealed that dolomite, which is the natural rock of $CaCO_3$ and $MgCO_3$, is a good heterogeneous base catalyst for the transesterification of PKO with methanol. The calcination of dolomite at 800 °C resulted in the mixed oxide of Ca and Mg that is active for the formation of methyl esters. Under the suitable conditions, the methanol/oil molar ratio of 30, the catalyst amount of 6 wt.%, and the reaction time of 3 h, the ME content of >98% was achieved at 60 °C. The calcined dolomite was reusable with the retention of the ME content higher than 90%. The biodiesel obtained possessed the physicochemical and fuel properties that meet the standard of diesel fuel and biodiesel issued by the Department of Energy Business, Ministry of Energy, Thailand.

Acknowledgements

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Mixed Oxides of Ca, Mg and Zn as Heterogeneous Catalysts for Methanolysis of Palm Kernel Oil

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Abstract

This work is to study the preparation of CaMgZn mixed oxides by co-precipitation. The mixed oxides were applied as a catalyst to transesterification of palm kernel oil with methanol. The catalysts were characterized by X-ray diffraction (XRD), X-ray fluorescence spectrometry (XRF), scanning electron microscopy (SEM) and temperature-programmed desorption of (CO_2-TPD). Reaction parameters such as amount of catalyst, molar ratio of oil to methanol and reaction time were optimized for the production of biodiesel. The highest activity was found for CaMgZn with the Ca:Mg:Zn molar ratio of 3:1:1 with the highest methyl ester content of 98%. The optimum conditions for the transesterification of palm kernel oil were the amount of catalyst of 6 wt.%, the methanol to oil molar ratio of 20, the temperature of 60 ^{o}C and the reaction time of 3 h.

Keywords: Mixed oxides, calcium oxide, zinc oxide, transesterification, palm kernel oil

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1. Introduction

The fossil fuels mainly crude oil, natural gas and coal have been playing an important role worldwide as the major energy resources. In recent years, the energy demand is increasing continuously because of the growth of population and the rapid development of industry and economics. Diesel fuel is a petroleum-based fuel, largely utilized in the area of transportation, agriculture, power generation and industries. However, the petroleum sources are limited and non-renewable. Moreover, the petroleum-derived fuels contain aromatics, organic sulfurs, and heavy metals. Their combustion emitts pollutants in the form of oxides of sulfur, oxides of carbon, particulate matter and unburnt hydrocarbons. Therefore, there is an urgent need to develop alternative fuels that are renewable, clean and economically feasible as a substitute to the petroleum diesel.

Biodiesel is a mixture of monoalkyl esters of long chain fatty acids derived from renewable feedstocks such as vegateble oils or animal fats [1]. It can be used directly in diesel engineswithout requiring engine modifications. Biodiesel is usually produced by transesterification of vegetable oils or animal fats with a monoalkyl alcohol (methanol or ethanol) in the presence of a catalyst. The catalysts most frequently used in the industrial biodiesel production are homogeneous basic catalysts, for example NaOH and KOH. The base-catalyzed transesterification can actively produce monoalkyl esters with a high yield under mild conditions. However, in the homogeneous process, removal of the soluble catalysts from the reaction mixture is difficult and generates a large amount of alkali wastewater during washing step. Heterogeneous catalysts can overcome these problems since they can be easily separated from the reaction mixture and reutilized, diminishing waste from the conventional process. Different heterogeneous base catalysts for the transesterification of vegetable oils have been reported in the literature. Most of them are supported alkaline metal oxide [2-5] alkaline-earth oxide [6-10], basic hydrotalcite [11-13], anion-exchange resins [14], and mixed metal oxides [15-18]. Recently, mixed metal oxides have attracted much attention for vegetable oil transesterification because of its tunable basicity by modifying the chemical composition and preparation procedure. Kawashima et al. [15] prepared A–B–O type metal oxides, where A is an alkaline-earth metal (Ca, Ba, Mg), alkaline metal, or rare earth metal (La) and B is a transition metal (Ti, Mn, Fe, Zr, Ce). It was found that CaZrO3 and CaO–CeO2 showed high transesterification activity and also showed high durability. The methyl ester yields were greater than 80% after 5-7 cycles of the reaction. Mg/La-mixed oxide catalysts catalyst was prepared by co-precipitation method and was investigated the transesterification activity [16]. The most active catalyst was obtained with Mg/La ratio of 3 with conversion close to 100%. Albuquerque et al. [17] evaluated the catalytic activity of different MgM (M = Al and Ca) oxides as solid base catalysts for transesterification process. The catalysts were prepared by co-precipitation method in a basic medium and subsequent calcination. The results demonstrated that the catalyst with a Mg:Ca molar ratio of 3.8 was the most active. This catalyst gives high FAME yield of 92%. Ngamcharussrivichai et al. [18] used mixed oxides of Ca and Zn as a solid base catalyst for transesterification of palm kernel oil with methanol. The catalyst was prepared by the co-precipitation method. The catalyst with a Ca/Zn molar ratio of 2.5 and followed by calcination at 800°C for 2 h exhibited the best catalytic activity for the transesterification. The activities of the Ca-Zn mixed oxides were compared with those of the CaO and ZnO. The methyl ester content reached 94% using Ca-Zn mixed oxides (Ca/Zn = 0.25) while the methyl ester content in the presence of CaO and ZnO were 46.2% and 1.7% respectively. This result emphasizes the advantage of co-existence of two different basic oxide components in the catalyst for transesterification.

The present work is an attempt to improve the physicochemical properties and the catalytic performance of the mixed oxides based on Ca and Zn for the transesterification of palm kernel oil. An introduction of magnesium into the mixed oxide is supposed to increase the basic properties, leading to an enhancement of the activity of the resultant mixed oxides. We have prepared the mixed oxides of Ca, Mg and Zn by pH-controlling co-precipitation method. Effects of various factors such as metal composition, aging time and aging temperature were studied to find suitable conditions for the catalyst preparation. The physicochemical properties of the mixed oxides were investigated by several techniques. The catalytic performance was studied in the transesterification of palm kernel oil with methanol under batch conditions. Moreover, the influences of reaction conditions on methyl ester (ME) content were investigated.

2. Experimental

2.1. Catalyst preparation

A mixed oxide of Ca, Mg and Zn was prepared by pH-controlling co-precipitation method. A required quantity of $Ca(NO_3)_2{\cdot}4H_2O$(Ajax Finechem)**,** $Mg(NO_3)_2{\cdot}6H_2O$ (Ajax Finechem) and $Zn(NO_3)_2{\cdot}6H_2O$ (Ajax Finechem) was dissolved in deionized water. The mixed metal solution was precipitated by adding an aqueous solution of Na_2CO_3 (CO_3^{2-}/metal ion = 0.75-1.5, $[CO_3^{2-}]$ = 0.5-1 M) under vigorous stirring. The pH of the resulting solution was maintained in the range of 7-8. The precipitate was further aged at room temperature or 60 °C for 8-20 h. Finally, the white solid was filtered, washed with deionized water, dried in an oven at 100 °C overnight, and calcined in a muffle furnace at 800 °C for 2 h. Hereafter, the mixed oxide catalysts were designated as CaMgZnXXX, where XXX represent the atomic ratio of Ca:Mg:Zn in the synthesis mixture.

2.2 Characterization

Oxide structure and cluster size of the synthesized CaMgZn mixed oxides were determined by techniques of powder XRD using a Rigaku DMAX 2200/Ultima+ diffractometer equipped with Cu Ka radiation. Elemental analysis was performed on a Philips PW-2400 ED-2000 Energy Dispersive X-ray Fluorescence Spectrometer (XRF). Morphological study was carried out with a JEOL JSM-5410 LV scanning electron microscope. The basic properties of the catalysts were investigated by the temperature programmed desorption (TPD) of CO_2 measurement using a Micromeritics AutoChem II 2920.

2.3 Transesterification procedure

A 250-mL three-neck round bottom flask equipped with a condenser and a magnetic stirrer was used as a reactor for transesterification of palm kernel oil. In a typical reaction, 0.6 g of a calcined catalyst was suspended in methanol. Temperature of the mixture was controlled at 60 °C by using a water bath. Then, palm kernel oil was added into the mixture under vigorous stirring. After the course of reaction (3 h), the catalyst was separated from the reaction mixture by centrifugation and the excess methanol was removed by using a rotary evaporation. Methyl ester layer was subsequently washed with deionized water and dried with Na_2SO_4. The methyl ester (ME) content, equivalent to methyl ester yield, was determined by a gas chromatograph (GC) equipped with a 30-m DB-Wax capillary column and a flame ionization detector (FID). Methyl ester (ME) content was calculated based on the standard method EN14103 using methyl undecanoate (C11) as the reference standard.

3. Results and Discussion

3.1 Characterization of CaMgZn mixed oxides

The elemental compositions of mixed oxides synthesized with different amounts of metal precursor are presented in Table 1. The Ca:Mg:Zn molar ratios found in the precipitated mixed oxides in all cases were deviated from those in the synthesis mixtures. It should be mainly attributed to the fact that Ca^{2+} and Mg^{2+} are precipitated at pH higher than the pH of synthesis mixture, while Zn^{2+} is readily precipitated at pH of 4 [15]. Therefore, the amount of Zn found in the resulting solid was highest. Although the amount of Mg in the synthesis mixture was increased to the ratio of 1:3:1, the solid with the Ca:Mg:Zn ratio of 1:1:1 was attained, suggesting the low precipitation of Mg^{2+}.

Powder X-ray diffraction patterns of the as-synthesized CaMgZn before and after calcination are presented in Fig. 1. As shown in Fig. 1a, as-synthesized CaMgZn exhibited peaks corresponding to $CaZn(CO_3)_2$ and $CaMg(CO_3)_2$ phases. This indicated that the as-synthesized CaMgZn were precipitated in the form of mixed carbonates of CaMg and CaZn. After calcination at 800 °C, decarbonation of the precursors lead to the formation of the corresponding metal oxides (CaO, MgO and ZnO). This fact is confirmed by XRD pattern, which are shown in Fig. 1b. Moreover, the diffraction peaks of $Ca(OH)_2$ were observed for CaMgZn mixed oxides, suggesting hydration of CaO by moisture in the atmosphere.

Fig. 2 showed the XRD patterns obtained from calcined CaMgZn precipitates with different Ca:Mg:Zn molar ratios. In the XRD pattern of MgZn11, the presence of MgO and ZnO phases was observed (Fig. 2a). The calcined CaMgZn showed the diffraction peaks related to CaO, MgO and ZnO phases (Fig. 2b-2e). By varying the metal composition, the diffraction peaks associated with the corresponding metal oxide species became more intense. For an exmple, the peak of MgO observed for CaMgZn131 possessed higher intensity than those found in MgZn11, CaMgZn111, CaMgZn113, and CaMgZn311.

The SEM images of as-synthesized CaMgZn precipitates with different Ca:Mg:Zn molar ratios are shown in Fig. 3. MgZn11 showed an aggregate of very small thin flake particles (Fig. 3a). In the presence of Ca, the formation of spherical particles with various sizes was observed (Fig. 3b-3d). The mixed precipitate particles of CaMgZn111 possessed non-uniform size and morphology (Fig. 3b). The presence of both flakes and spheres with a wide range of size distribution can be seen. The increase in the Ca content, CaMgZn311 (Fig. 3c), uniformly reduced the particle sizes to 2-3 µm. Similarly, compared to CaMgZn111 (Fig. 3b), CaMgZn131 with increasing amount of Mg exhibited much smaller particle sizes (ca. 1 µm) (Fig. 3d). On the other hand, the morphology of CaMgZn113 (Fig. 3e-3f) was an aggregate of flake-like particles similarly to that of MgZn11 (Fig. 3a). However, the incorporation of Ca distorted of the particle shape to shortened and thick pellets (Fig. 3f).

To investigate the effect of catalyst preparation on the catalyst morphology, the calcination temperature was studied between 500 °C and 800 °C. Fig. 4a showed SEM image of uncalcined sample. It was found that the spherical particles were formed by an aggregation of small thin flake particles. After calcination, the merging of thin flake particles occurred. Increase of the calcination temperature from 500 °C to 800 °C caused an increase in the merging of thin flake particles (Fig. 4b-4e). The influences of the aging conditions on the morphology of mixed precipitates before and after the calcination are illustrated in Fig. 5a-5f. Aging the synthesis mixture at 60 °C for 8 h resulted in CaMgZn precipitate with small spherical particles of of 0.7-1 µm (Fig. 5a). The particle size of CaMgZn precipitate was increased when the aging time was extended to 20 h as shown in Fig. 5c (ca. 3 µm). It should be due to the aggregation of very small thin flake particles to form larger spheres. When CaMgZn precipitate was aged at room temperature for 20 h, the particle size was decreased to less than 0.5 µm (Fig. 5e). It can be seen that the low aging temperature retarded the processes of precipitation of metal ions and the aggregation of precipitate nuclei, yielding uniform defect spheres. In all the cases, after the calcination, the particle sizes of resulting CaMgZn mixed oxides were smaller than those of the parent ones (Fig. 5b, 5d and 5f), implying a considerable loss of CO2 via the decarbonation. It is likely that these small spheres were derived from the decomposition of the aggregate thin flakes.

3.2 Transesterification over CaMgZn mixed oxides catalysts

The methanolysis of palm kernel oil was chosen as a reaction to evaluate the catalytic activity of the CaMgZn mixed oxides, since this is of commercial significance in the production of biodiesel. Table 2 showed Methyl esters (ME) content attained over calcined CaMgZn prepared with different Ca:Mg:Zn molar ratios. It can be seen that the catalyst consisting of only Mg and Zn was not active for the formation of methyl esters. It should be due to low basicity of MgO and ZnO themselves. With increasing the amount of Ca, CaMgZn311, the highest ME content of 98.0% can be attained. CaO is considered as the main basic sites responsible for the transesterification over the mixed oxides of CaZn [15], since it possesses the highest basicity (H_26.5) [10]. It is interesting to note that an increase in the fraction of Mg (CaMgZn131) hampered the transesterification to larger extent than the case of Zn (CaMgZn113). Ngamcharussivichai et al. suggested that ZnO promoted the methyl ester synthesis over CaZn catalysts by reducing the particle size of the resultant mixed precipitates and facilitating the thermal decomposition of carbonate species to easily form the active CaO sites [15].

The temperature-programmed desorption of CO2 was used to get information about the basicity of the most active CaMgZn311. The CO2 desorption profiles from the temperature-programmed desorption (TPD) analysis are shown in Fig. 6. A broad peak of MgZn11 (Fig. 6a) was observed between 100 and 320 °C, which can be attributed to CO2 desorbed from the basic ZnO. The desorption peak at 237 °C is attributed to the interaction of CO2 with weak basic. The presence of weak basic sites resulted in the low activity for transesterification. Pure calcium oxide derived from CaCO3 showed a desorption peak at 660 °C (Fig. 6b). CaMgZn111 and CaMgZn131 exhibited a similar desorption profile (Fig. 6c and 6e, respectively). The peaks located at 630 °C were ascribed to the desorption of CO2 from the basic CaO sites. Moreover, it was found that the desorption peak slightly shifted to the lower temperatures when compared to pure CaO. CaMgZn113 showed the peak related to CO2 desorbed from CaO at 632 °C, while the desorption peak appearing at 190 °C corresponded to ZnO (Fig. 4f). CaMgZn311 (Fig. 6d) possessed two desorption peaks, which indicated the presence of at least two types of basic sites with different strengths. It should be related to the high Ca content. These results show that CaMgZn311 exhibits high transesterification activity compared to the other catalysts. The high activity is due to the presence of a large number of strong basic sites in the CaMgZn311 catalyst.

Finally, CaMgZn311 was selected to be evaluated in the transesterification in order to determine the optimum reaction conditions. The influence of three parameters on palm kernel oil transesterification was examined: catalyst amount, methanol to oil molar ratio, and reaction time. The influence of the catalyst amounts was studied at a 20:1 molar ratio of methanol to palm kernel oil at 60 °C for 3 h. The catalyst amount was varied in the range of 2-8 wt.%. As shown in Fig. 7, the methyl ester content was increased with the increase of catalyst amount from 2 to 6 wt.%. However, with further increase in the catalyst amount the methyl ester content was decreased, which was possibly due to a mixing problem involving reactants, products and solid catalyst.

Stoichiometrically, the methanolysis of vegetable oil required three moles of methanol for each mole of oil. However, in practice, the molar ratio of methanol to oil should be higher than that of stoichiometric ratio in order to drive the reaction towards completion and produced more methyl ester as product. As shown in Fig. 8, with an increase in the molar ratio of methanol to oil, the methyl ester content was increased considerably. The highest methyl content was obtained when the molar ratio was 20:1.

The methyl ester content with various reaction times was shown in Fig. 9. The reaction time was varied in the range 0.5-4 h. As can be seen from Fig. 10, the methyl ester content was increased in the reaction time range between 0.5 and 2 h, and thereafter remained nearly constant as a result of near-equilibrium conversion; the maximum methyl ester content was achieved after 2h.

4. Conclusions

In summary, CaMgZn mixed oxide catalysts with different Ca:Mg:Zn molar ratios were synthesized via co-precipitation method. The XRD results indicated that the as-synthesized CaMgZn were precipitated in the form of mixed carbonates of CaMg and CaZn, and after the calcination the corresponding metal oxides were obtained. The as-synthesized CaMgZn morphologies showed the aggregation of small thin flakes to spherical particles with various sizes. The particle sizes of the spheres strongly depended on the aging time and aging temperatures.

The catalyst with the Ca:Mg:Zn molar ratio of 3:1:1 showed the highest activity in the transesterification of palm kernel oil with methanol. When the reaction was carried out at 60 oC, with a molar ratio of methanol to oil of 20, a reaction time of 6 h and a catalyst amount of 6 wt.%, the highest methyl ester content reached 98%.

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Table 1 Elemental composition of calcined CaMgZn catalysts prepared with different Ca:Mg:Zn molar ratios

Catalyst	Ca:Mg:Zn molar ratio[a]		Metal composition in the solid (wt.%)		
	Mixture[b]	Solid[c]	CaO	MgO	ZnO
MgZn11	0:1:1	0:1:4	0.0	10.7	89.2
CaMgZn111	1:1:1	6:1:7	37.9	4.0	58.0
CaMgZn311	3:1:1	19:1:7	63.1	2.3	34.6
CaMgZn131	1:3:1	1:1:1	29.8	20.4	49.6
CaMgZn113	1:1:3	1:1:4	17.9	9.6	72.3

[a] Determined by XRF spectroscopy.

[b] Ca:Mg:Zn molar ratio in the synthesis mixture.

[c] Ca:Mg:Zn molar ratio in the final solid.

Table 2

Methyl esters (ME) content[a] attained over calcined CaMgZn prepared with different Ca:Mg:Zn molar ratios

Catalyst	$\frac{\text{Ca}}{(\text{Ca+Mg+Zn})}$	ME content[a] (wt.%)
MgZn1	0	3.1
CaMgZn111	0.36	21.1
CaMgZn311	0.60	98.0
CaMgZn131	0.33	49.5
CaMgZn113	0.15	87.1

[a] Transesterification conditions: catalyst amount, 6 wt%; methanol/oil molar ratio, 20; temperature, 60 °C; time, 3 h.

Figure Captions

Fig. 1. XRD patterns of CaMgZn111 before (a) and after (b) the calcination at 800 °C. (Symbols: (▼) $CaZn(CO_3)_2$, (⬣) $CaMg(CO_3)_2$, (✦) $Mg(OH)_2$, (◆)$Zn(OH)_2$, (●) CaO, (▲) $Ca(OH)_2$, (⧗) MgO and (■) ZnO).

Fig. 2. XRD patterns of CaMgZn precipitates prepared with different Ca:Mg:Zn molar ratios after the calcination at 800°C: (a) MgZn11, (b) CaMgZn111, (c) CaMgZn311, (d) CaMgZn131, and (e) CaMgZn113. (Symbols: (●) CaO, (▲) $Ca(OH)_2$, (⧗) MgO and (■) ZnO).

Fig. 3. SEM images of as-synthesized CaMgZn precipitates prepared with different Ca:Mg:Zn molar ratios: (a) MgZn11, (b) CaMgZn111, (c) CaMgZn311, (d) CaMgZn131, (e) CaMgZn113 and (f) CaMgZn113 (x15,000).

Fig. 4. SEM images of CaMgZn111 (a) before and after the calcinations at (b) 500°C, (c) 600°C, (d) 700°C, and (e) 800°C.

Fig. 5. SEM images of CaMgZn precipitates aged at different and temperatures and times: (a) uncalcined CaMgZn111 (60 °C, 8 h), (b) calcined CaMgZn111 (60 °C, 8 h), (c) uncalcined CaMgZn111 (60 °C, 20 h), (d) calcined CaMgZn111 (60 °C, 20 h), (e) uncalcined CaMgZn111 (rt, 20 h), and (f) calcined CaMgZn111 (rt, 20 h).

Fig. 6. CO_2-TPD analysis of calcined CaMgZn catalyst prepared with different Ca:Mg:Zn molar ratios: (a) MgZn11 , (b) CaO (from $CaCO_3$), (c) CaMgZn111, (d) CaMgZn311, (e) CaMgZn 131, and (f) CaMgZn113.

Fig. 7. Dependence of methyl ester (ME) content on catalyst amount over CaMgZn311-I. Reaction conditions: methanol/oil molar ratio, 20:1; temperature, 60°C; time, 3 h.

Fig. 8. Dependence of methyl ester (ME) content on methanol/oil molar ratio over CaMgZn311-I. Reaction conditions: catalyst amount, 6 wt.%; temperature, 60°C; time, 3 h.

Fig. 9. Dependence of methyl ester (ME) content on reaction time over CaMgZn311-I. Reaction conditions: catalyst amount, 6 wt.%; temperature, 60°C; methanol/oil molar ratio, 16

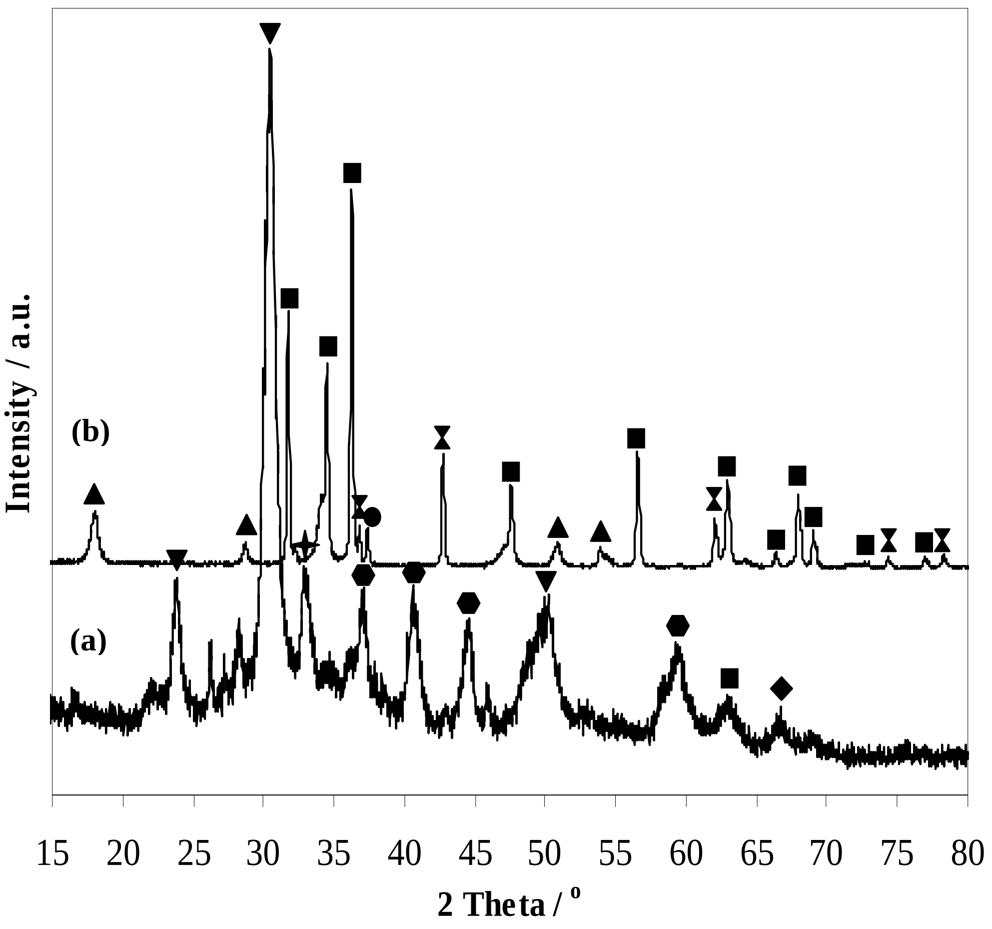
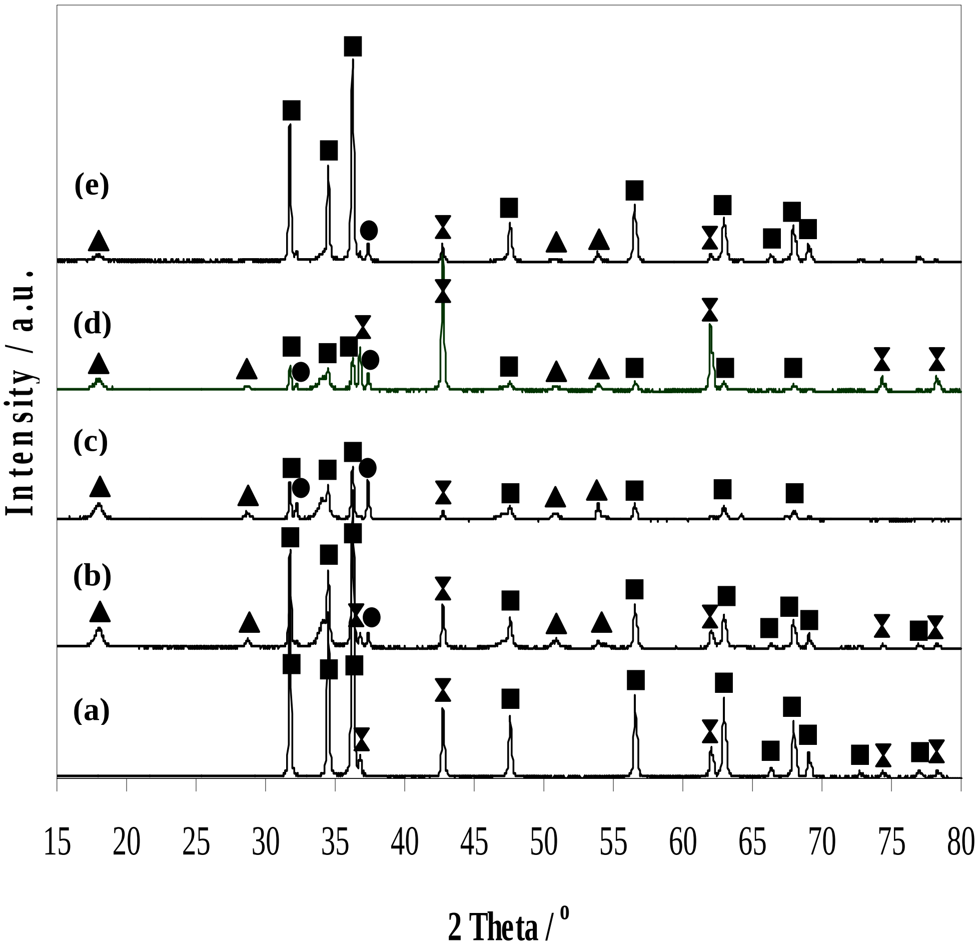


Fig. 1


(e)
(d)
(c)
(b)
(a)
Intensity / a.u.
15
20
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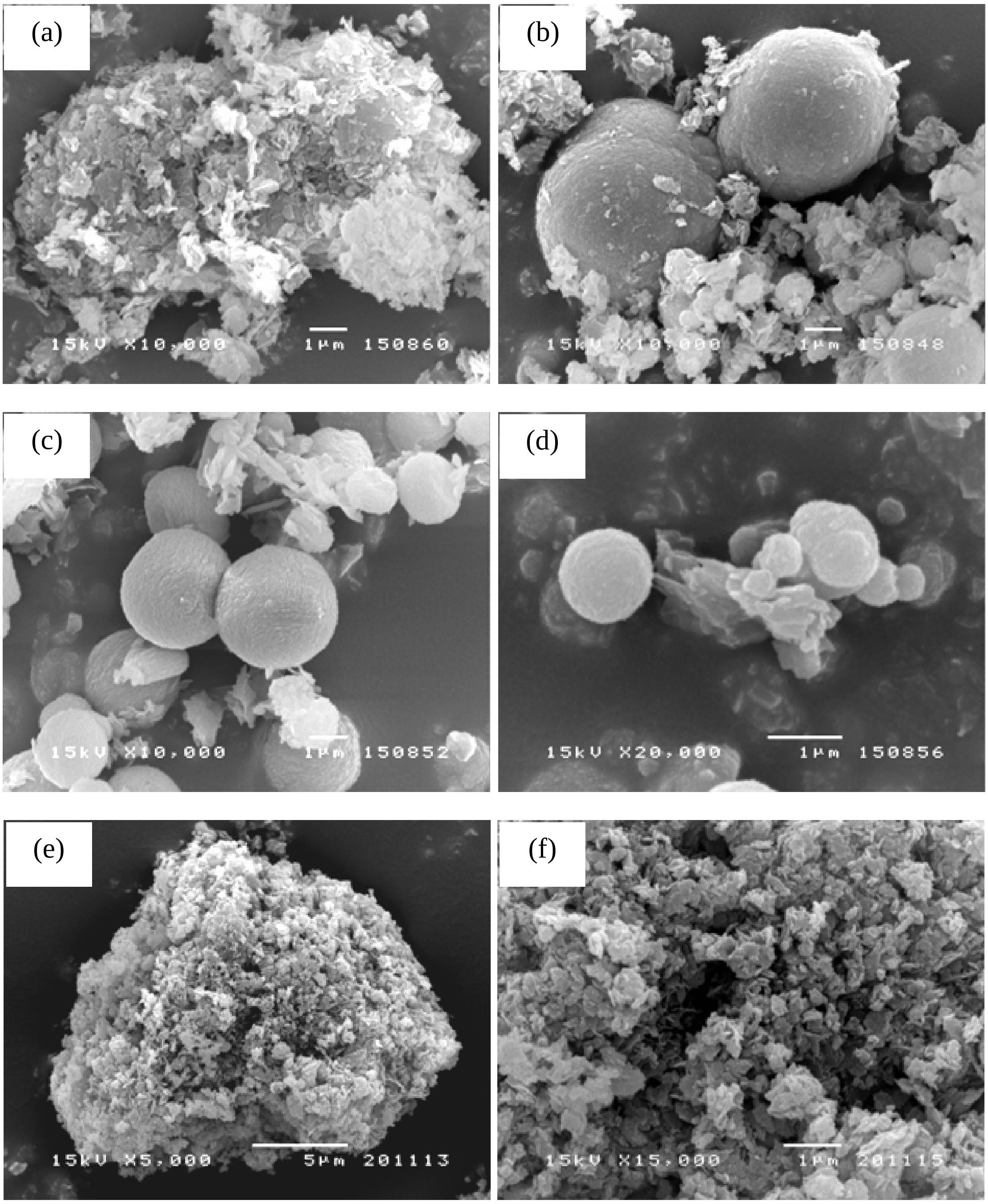
75
80
2 Theta / o

Fig. 2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(b)
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(c)
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(e)
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(f)
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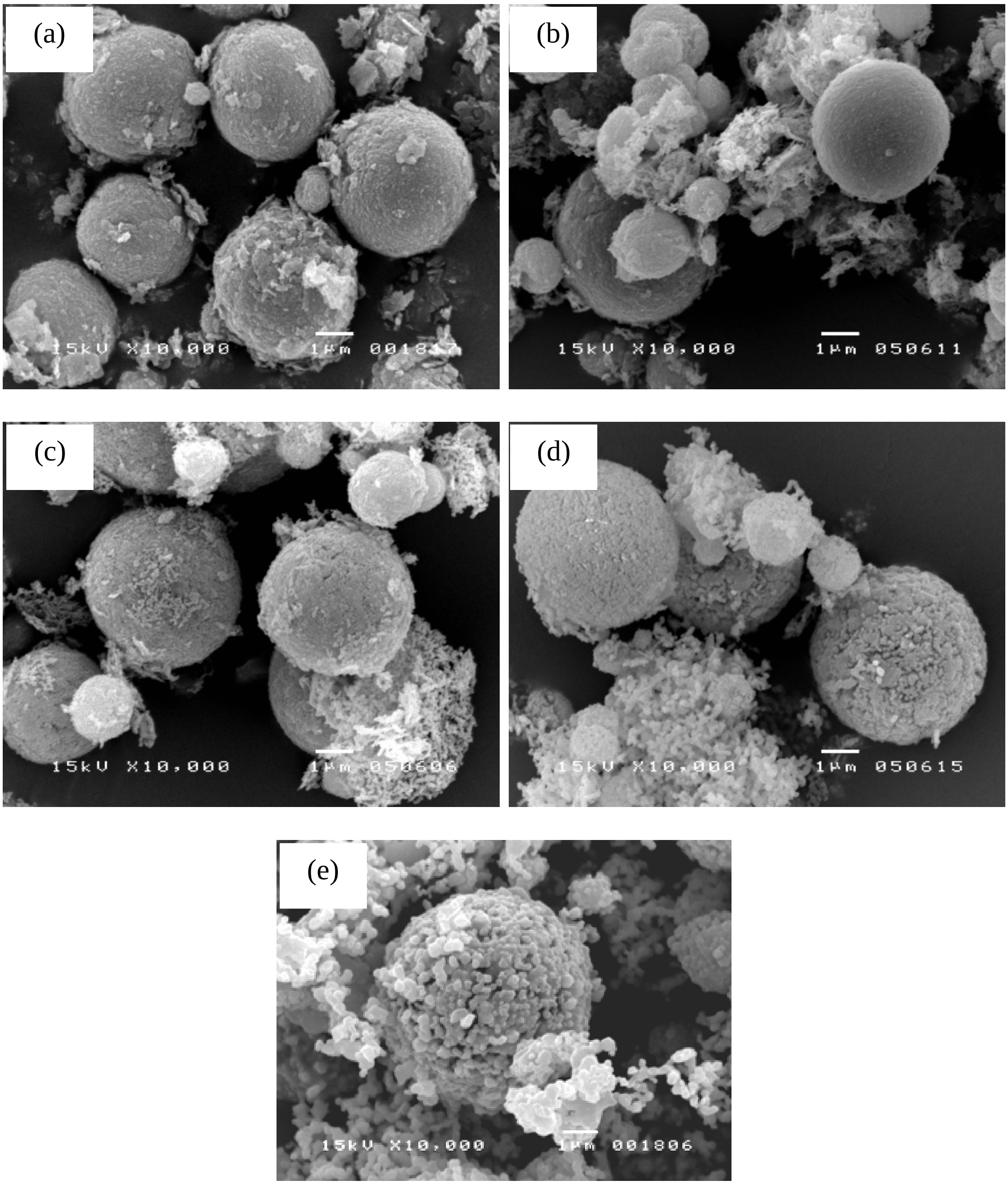
Fig. 3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(d)
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Fig. 4

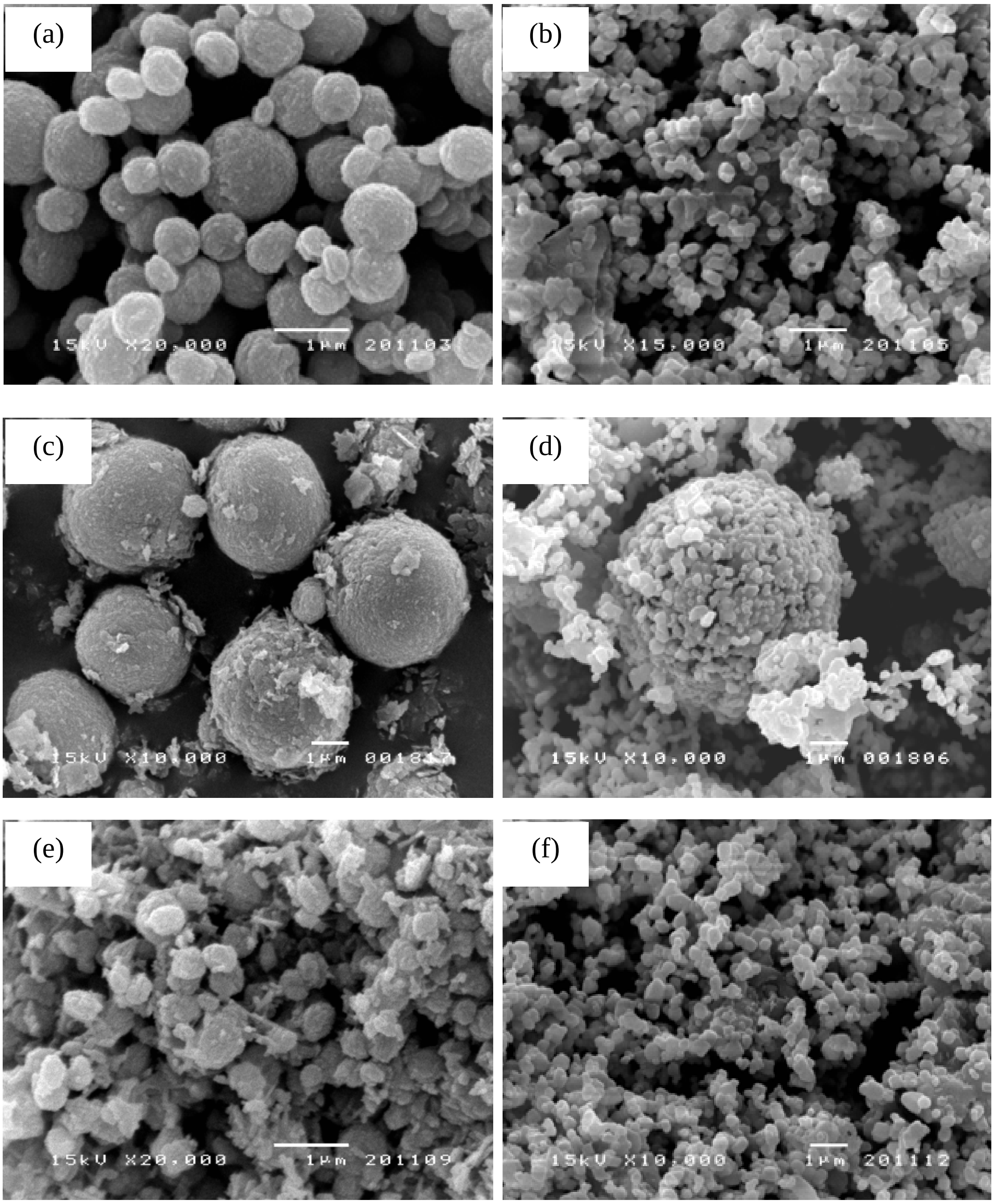
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Fig. 5

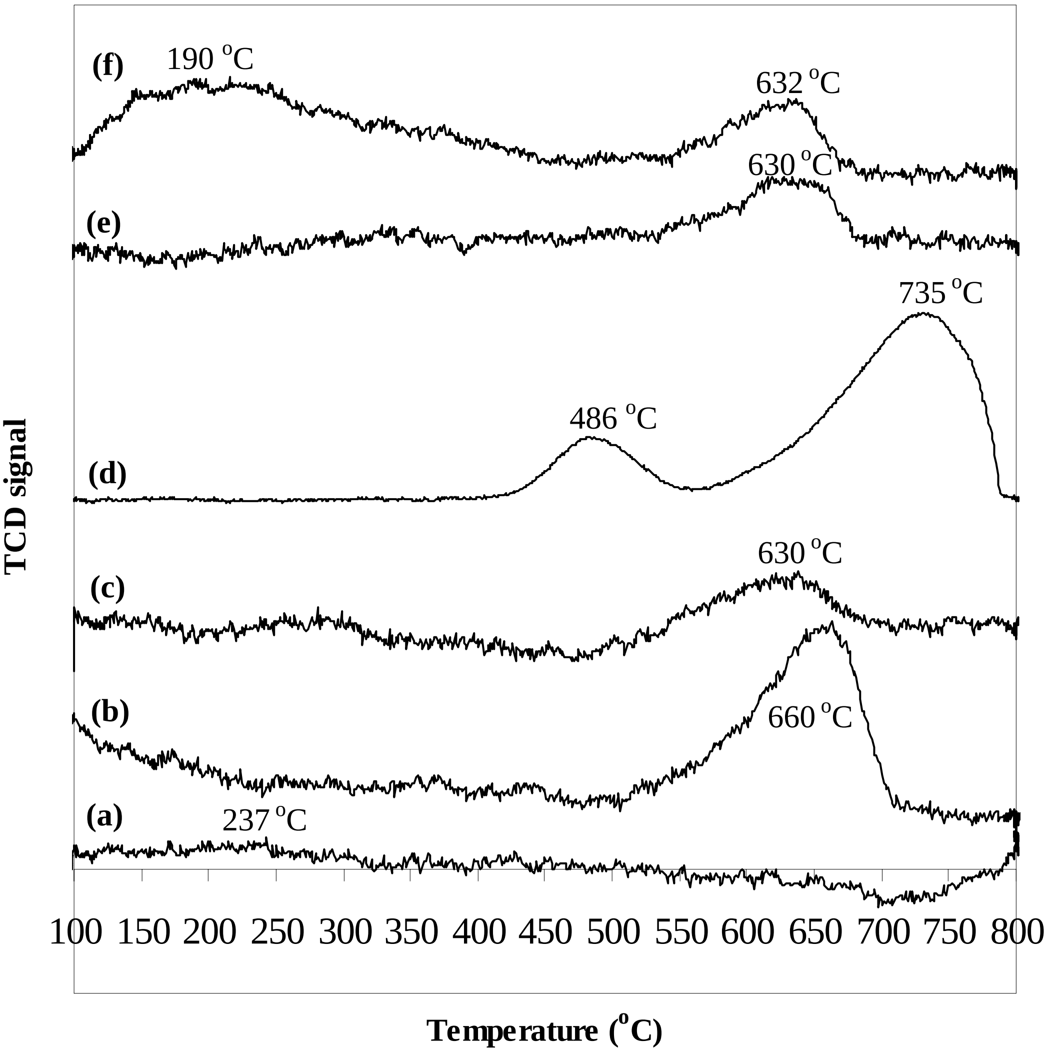
(f)
190 °C
632 °C
630 °C
(e)
735 °C
486 °C
(d)
TCD signal
630 °C
(c)
(b)
660 °C
(a)
237 °C
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
Temperature (°C)

Fig. 6

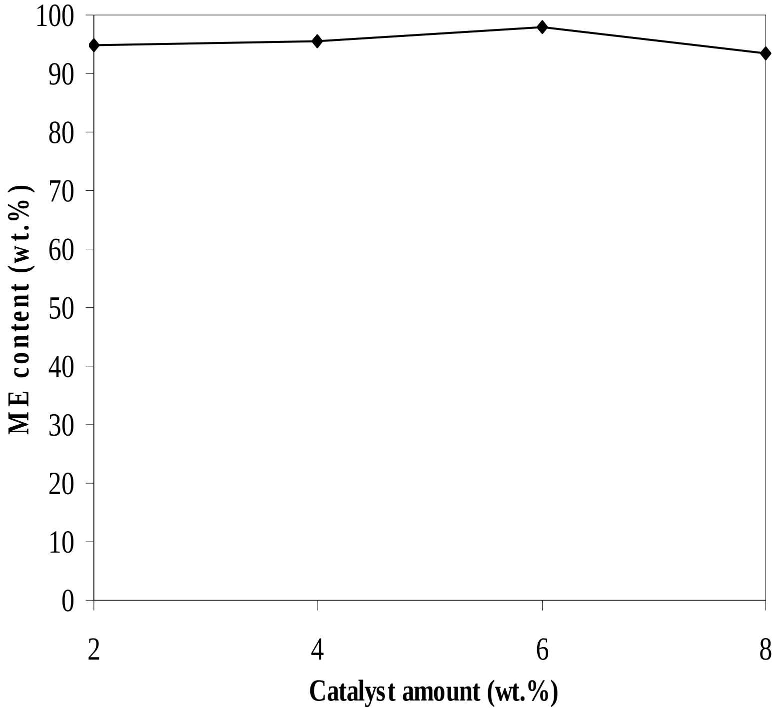
100
90
80
70
60
50
40
30
20
10
0
ME content (wt.%)
2
4
6
8
Catalyst amount (wt.%)

Fig. 7

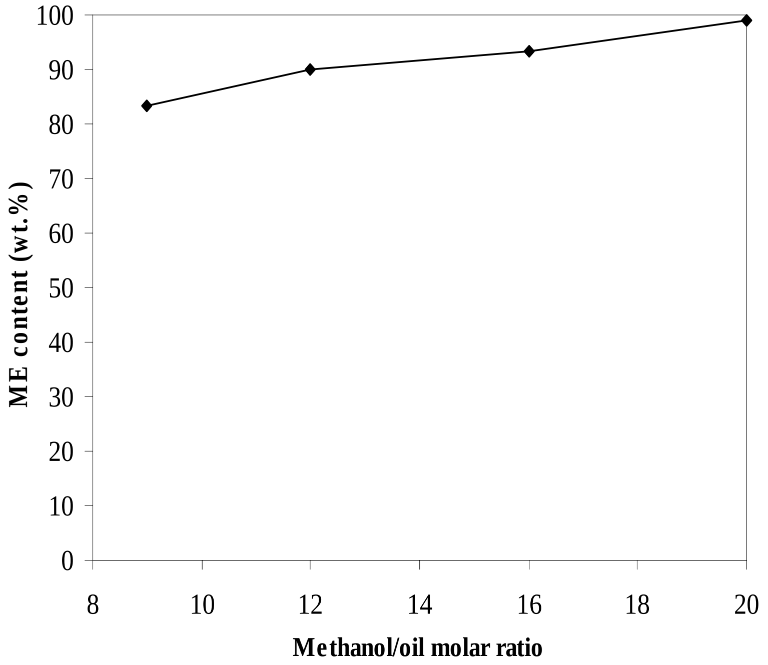
100
90
80
70
60
50
40
30
20
10
0
ME content (wt.%)
8
10
12
14
16
18
20
Methanol/oil molar ratio

Fig. 8

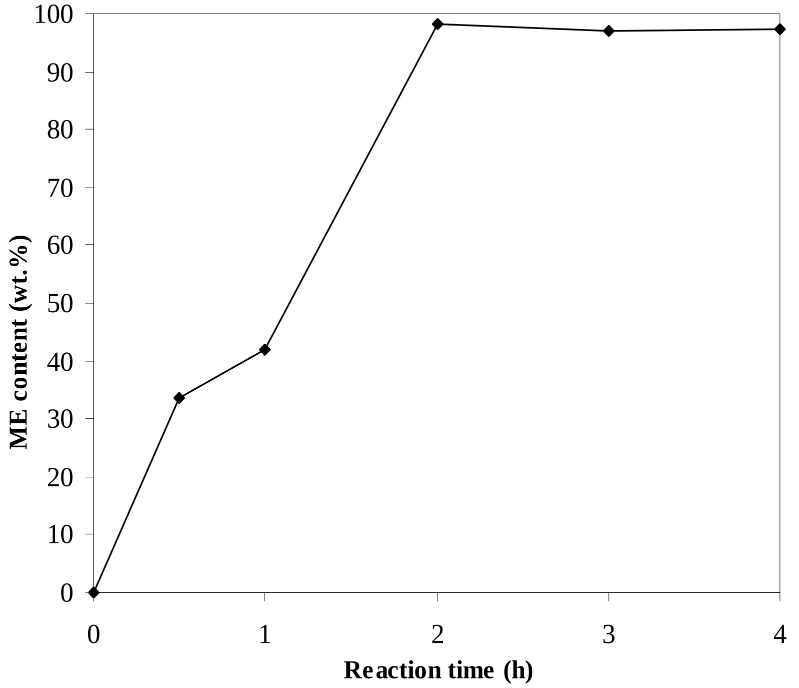
100
90
80
70
60
50
40
30
20
10
0
ME content (wt.%)
0
1
2
3
4
Reaction time (h)

Fig. 9

Ca-based three-component mixed oxides as heterogeneous base catalysts for methanolysis of palm kernel oil

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Abstract

Several three-component mixed metal oxides have been prepared and tested in the transesterification of palm kernel oil with methanol. Ca was set as the main catalytically active component, while the other two metals selected from Mg, Ba, Zn and Al were incorporated to alter the physicochemical properties and the catalytic performance of the resultant mixed oxides. The synthesis of the mixed oxides was performed according to a pH-controlling co-precipitation method using the corresponding metal nitrates as the metal precursors and Na_2CO_3 as the precipitant. The catalyst characterization was carried out by using various techniques, including N_2 adsorption-desorption measurement, X-ray fluorescence spectroscopy, X-ray diffraction, scanning electron microscopy, thermogravimetric/differential thermal analysis and temperature-programmed desorption of CO_2. The methanolysis of palm kernel oil was studied batchwise at 60 C and 1 atm. The influences of the metal types and the calcination temperatures were investigated. Leaching of the active components and the catalyst reusability were also studied.

Keywords: Biodiesel, Transesterification, Mixed oxide, Heterogeneous catalyst

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1. Introduction

Biodiesel, a mixture of alkyl esters, is a non-toxic, clean, biodegradable and renewable fuel that can be easily produced from the transesterification of vegetable oils or animal fats with small alcohols, such as methanol. Conventional biodiesel production is carried out in the presence of homogeneous base catalysts, e.g. hydroxides and methoxides of Na or K. The high conversion of the oils can be achieved in a short period. Since the residual base in the esters affects the quality of biodiesel as a fuel for diesel engines, the ester phase must be thoroughly washed in many successive stages to remove the catalyst, releasing a large amount of alkaline wastewater. Moreover, there is a loss of the ester yield due to saponification and emulsification via hydrolysis of the esters produced.

The transesterification over heterogeneous base catalysts is a promising route for a green production of biodiesel. Suppes et al. applied natural calcium carbonate rock as a transesterification catalyst [1]. Due to its low basicity, the high reaction conditions (T > 200 °C and P > 30 bar) were required to achieve the oil conversion of > 95%. Al_2O_3-supported alkali metal catalysts exhibited much higher activity [2]. However, the XRF study revealed a serious leaching of the active species into the reaction mixture [3], resulting in a remarkable loss of the methyl ester yield in the successive runs. Mixed oxides derived from MgAl hydrotalcites were studied in the transesterification of triglycerides from the various sources with methanol [4-6]. Recently, Institut Français du Pétrole (IFP) has successfully commercialized new biodiesel production plant based on heterogeneous catalysis technology [7]. A spinel mixed oxide of zinc and aluminum is used as the catalyst, which promotes the reaction without loss of active components. However, as a consequence of relatively low basicity, the process is carried out at much higher methanol/oil ratio and higher temperature and pressure when compared to the conventional process.

The severe drop of the catalytic performance, caused by the leaching effect, may be avoided by employing a catalyst in the form of mixed oxides. Alkali earth metal oxides, especially MgO and CaO, are less soluble in methanol than highly basic alkali metal oxides [8]. Ca-Mg mixed oxide derived from the natural dolomitic rock exhibited high activity in the methanolysis [9,10]. The oxides combined from Ca and Zn, prepared by a co-precipitation method, possessed very small particle sizes and relatively high surface area in comparison with the pure component oxides [11]. Moreover, the formation of the mixed precipitate reduced the activation temperature by which the transesterification was rapidly promoted over the catalyst calcined at temperature < 800 °C. Other mixed oxides, for example $CaO \cdot MgO$ [12], $K_yMg_{1-x}Zn_{1+x}O_3$ [13], synthesized by different procedures were also investigated in the methanolysis.

Calcium carbonate has three kinds of crystal polymorphs, i.e. vaterite, aragonite, and calcite, with rhombohedral, orthorhombic and hexagonal structures, respectively, from which calcite is the most stable and vaterite the least stable phase. A number of literatures dealt with the influences of divalent ions on the nucleation or the growth rate of $CaCO_3$ polymorphs [14-17]. For example, Zn^{2+} strongly suppresses the growth of calcite by adsorption on kink sites, resulting in the formation of small particles [14,15], whereas Mg^{2+} forms Mg-calcite structure $(Mg_xCa_{1-x})CO_3$ with variable Mg contents [15-17]. Our previous study suggested that the $CaCO_3$ polymorphs existing in different natural Ca-based materials, i.e. cuttlebone, dolomite and calcite, influenced the catalytic properties of the resulting oxides in the methanolysis. It was likely to be due to the different conditions required to activate each carbonate material.

In the present work, several Ca-based three-component oxides derived from the calcination of the corresponding mixed carbonate precipitates of Ca combined with other two metals, selected from Mg, Ba, Zn and Al, were investigated for their physicochemical and the catalytic properties. The morphology of the oxides was largely influenced by the types of metal ions. Among the mixed oxides studied, a mixed oxide of Ca, Mg and Zn (CaMgZn) showed a superior performance in the catalytic transesterification of palm kernel oil with methanol. The effects of calcination temperatures and regeneration methods for CaMgZn were also studied.

2. Material and Methods

2.1 Catalyst preparation

One-, two- and three-component oxide catalysts were prepared according to the conventional co-precipitation of aqueous solutions of corresponding metal precursors and precipitant. The precursors used were nitrate salts of di- and tri-valent metals, including $Mg(NO_3)_2.6H_2O$, $Ca(NO_3)_2.4H_2O$, $Ba(NO_3)_2$, $Zn(NO_3)_2.6H_2O$, and $Al(NO_3)_3.9H_2O$ (AR grade, Ajax Finechem). Na_2CO_3 (AR grade, Ajax Finechem) was used as the precipitant. For a typical catalyst preparation, required amounts of the metal precursors were completely dissolved in deionized water and then slowly mixed with an aqueous solution of carbonate salt under vigorous stirring at ambient temperature. The molar ratio of CO_3^{2-}/metal ions was kept at 1.5. The pH of the solution was fixed between 7 and 8. The resulting mixture was aged overnight (~20 h) at 60 °C. The solid product was recovered by filtration, followed by washing with deionized water and drying in an oven at 100 °C overnight. Before being applied as a catalyst, the dried solid was calcined in a muffle furnace at temperatures of 800 °C for 2 h.

2.2 Characterization

Oxide structures of the synthesized mixed oxides were determined by techniques of powder X-ray diffraction (XRD) using a Bruker D8 ADVANCE diffractometer equipped with Cu Kα radiation. Assignments of diffraction peaks were consulted with the JCPDS powder diffraction files. Elemental analysis was performed on an Oxford ED-2000 energy dispersive X-ray fluorescence (XRF) spectrometer. Morphological study was carried out with a JEOL JSM-5800LV scanning electron microscope (SEM). A Perkin Elmer Pyris Diamond thermogravimetry (TG/DTA) was used for thermogravimetric analysis (TGA) at a temperature ramp rate of 8 °C min^{-1} under dry air flow with the rate of 20 mL min^{-1}. Textural properties of mixed oxides were measured by techniques of N_2 physisorption using a Micromeritic ASAP 2020 surface area and porosity analyzer. Calculation of surface area was based on the BET equation using the linear–relationship data attained in the P/P_0 range of 0.02–0.2. A Micromeritic Autochem II was employed for determining basicity of the catalysts by means of temperature-programmed desorption (TPD) of CO_2. The adsorption of CO_2 (10 mol.% in Ar) was carried out at 100 °C and the desorption step was performed at the temperature ramp rate of 10 °C min^{-1} under Ar flow. The peak areas were deconvoluted by using an IGOR Pro 5.04B.

2.3 Transesterification procedure

Refined bleached deodorized palm kernel oil (PKO) was donated by Chumporn Palm Oil Industry Co., Ltd. Acid value and moisture content of the oil were less than 2.49 $mg_{KOH}\ g^{-1}_{oil}$ and 0.1 wt.%, respectively. The reaction was carried out in a 100-mL 2-neck round bottom flask equipped with a condenser and a magnetic stirrer. Typically, 1 g of calcined catalyst was suspended in a required volume of methanol (99.5 %, commercial grade). Temperature of the mixture was controlled at 60 °C by a water bath. Subsequently, the oil was added into the mixture under vigorous stirring. After the course of the reaction, the catalyst was separated by centrifuge and the reaction mixture was then loaded into a rotary evaporator to remove excess methanol. The methyl ester layer was recovered in a separating funnel. The composition of methyl ester product was analyzed with a Varian CP-3800 gas chromatograph (GC) equipped with a FID detector and a 30-m DB-Wax capillary column. The amount of methyl esters formed was calculated based on the internal standard method using methyl undecanoate as a reference. The accuracy of this method was confirmed by comparing the data with those obtained according to the standard method of EN14103. The methyl ester (ME) content is defined as follows:

$$\text{ME content (wt.\%)} = \frac{\text{Caculated weight of methyl esters}}{\text{Weight of methyl ester phase}} \times 100$$

3. Results and discussion

Table 1 shows the ME contents obtained from the transesterification of PKO catalyzed by various one-component oxides. Under the present conditions, MgO did not active, while the ME content of 46.2 % was attained over CaO. These results are consistent with the previous work by Peterson et al. who reported the low catalytic activity of MgO and moderate methyl ester yield over CaO in the transesterification of rapeseed oil [18]. Surprisingly, the methyl ester formation over the synthesized BaO was very low. It should be related to the temperature required for the activation of Ba precipitate. The TG analysis suggested that the decomposition of $BaCO_3$ begins at > 850 °C. Therefore, the calcination of Ba precipitate at 800 °C was not sufficient to generate BaO sites. Pure ZnO gave very low ME content due to its low basicity. On the other hand, the high ME content of 82.2 was achieved over the calcined Al precipitate.

Al_2O_3, especially in γ phase, is widely used as a support for the active transesterification catalysts. However, Al_2O_3 itself did not possess the activity [2]. The formation of sodium oxide as well as basic aluminate species, for example $NaAlO_2$, was possible upon the calcination of Al precipitate. Contreras et al. observed transition alumina and $NaAlO_2$ after the calcination of sodium dawsonite ($NaAl(OH)_2CO_3$), precipitated from a mixture of aluminum sulfate and sodium carbonate, at temperatures of 400-700 and 800-900 °C, respectively [19].

$$
\begin{array}{ccccc}
NaAl(OH)_2CO_3 & \xrightarrow{400^\circ C-700^\circ C} & \begin{matrix} Na_2O + Al_2O_3 \\ + CO_2 + H_2O \end{matrix} & \xrightarrow{800^\circ C-900^\circ C} & NaAlO_2 \\
\textit{Sodium dawsonite} & & \textit{Transition alumina} & & \textit{Sodium aluminate}
\end{array}
$$

The test of commercial $NaAlO_2$ in the transesterification of PKO resulted in the ME content of 94%, but a part of the catalyst dissolved in methanol concomitantly with the formation of soap. This result suggested that the reaction over the calcined Al precipitate significantly undergoes through the homogeneous pathway.

The elemental composition and the physicochemical properties of calcined two-component oxides are summarized in Table 2. The oxides possessed low specific surface area due to the absence of intraparticle porosity, even though their particle sizes were small. MgAl and ZnAl had relatively high surface area of 60 and 51.6 $m^2\ g^{-1}$, respectively, which is in the typical range for the mixed oxides with spinel structure [20]. The XRD analysis indicated the presence of poor crystalline spinel phase in the form of $MgAl_2O_4$ and $ZnAl_2O_4$. The oxides of MgAl and ZnAl exhibited high activity in the formation of methyl esters while the rest gave the ME content less than 18%. Taking into account a high Na content of MgAl and ZnAl, it is likely that a part of Al precipitated in the form of sodium dawsonite after which was converted to transition alumina as well as $NaAlO_2$ upon the calcination as mentioned above.

When Ca was added into the synthesis mixtures, the resulting solids possessed the surface areas lower than the corresponding two-component oxides (Table 3). This effect was very pronounced in the case of CaMgAl and CaZnAl. Compared to the SEM images of the two-component oxides, an aggregation of small particles in the presence of Ca was found (Fig. 1). CaMgZn formed large spheres with the size of ca. 6 μm (Fig. 1B), similarly to the framboidal vaterite aggregates [21,22], while a part of CaZnAl particles exhibited rod-like shape (Fig. 1F). The combination of Ba with Mg and with Zn resulted in the formation of relatively large particles (Table 2). Ca induced merging of BaZn particles (Fig. 1D). It seemed that the crystallization of calcite was disturbed by the divalent metal ions via either the adsorption on the kink sites or the incorporation in to the lattice [14-17], leading to the distortion of the ideal morphology.

It was revealed by the XRD analysis that the mixed divalent metal ions were precipitated in the form of mixed metal carbonates (Fig. 2(a)). The broad characteristics of the patterns of CaMgZn precipitate, indicating its low crystallinity, can be explained by the incorporation of Mg^{2+} and Zn^{2+} into the lattice of $CaCO_3$. Loste et al. observed that the transformation of amorphous calcium carbonate into the crystalline phases was retarded at the high concentration of Mg^{2+} [17]. The remaining Mg^{2+} and Zn^{2+} were precipitated as the hydroxide species due to the limit of CO_3^{2-} concentration. After the calcination at 800 °C, the carbonates and the hydroxides were entirely decomposed, giving the corresponding metal oxides. The cluster size of CaO in the case of CaMgZn was smallest (Table 3). We reported a decrease in the CaO cluster size with increasing the Zn content in the mixed oxides of Ca and Zn [11]. The generation of CaO with nanosize as a result of the thermal treatment of dolomite ($CaMg(CO_3)_2$) was observed by Wilson et al [10]. The $Ca(OH)_2$ phase appearing in the pattern should be a product of CaO hydrolysis by moisture in the atmosphere (Fig. 2(b)).

The formation of CaZn mixed precipitate significantly reduced the temperature required for the generation of CaO [11] (*see* also Fig. 3C). The liberation of CO_2 from $CaCO_3$ was facilitated by a number of voids produced via the earlier decomposition of basic Zn carbonate species. When compared to pure $CaCO_3$ (Fig. 3A), the weight loss attributed to the decarbonation of $CaCO_3$ (> 700 °C) occurred at lower temperatures in the case of the mixed precipitates. CaMgZn precipitate had the lowest decomposition temperature of 706 °C (Fig. 3D). The generation of MgO occurred at 420-460 °C, while the dehydration of $Ca(OH)_2$ was usually observed at temperatures lower than 550 °C. Therefore, the presence of the weight loss at 622 °C suggested that there was other $CaCO_3$ locating in the different environment to that decomposed at 706 °C (Fig. 3D). This result was in accordance with the XRD analysis that indicated the existence of two mixed Ca carbonates, i.e. $CaMg(CO_3)_2$ and $CaZn(CO_3)_2$ (Fig. 2). By consulting Fig. 3B and 3C, CaO from the mixed carbonate of Ca and Zn should take place at the lower temperature (622 °C).

Except for CaMgAl and CaZnAl, the presence of Ca enhanced the synthesis of methyl esters (Table 3). It should be due to the basicity of CaO [23]. The low-energy ion scattering (LEIS) study indicated that Ca deposited above the tetrahedral Zn in the spinel structure, resulting in the low activity of Ca doped $ZnAl_2O_4$ [20]. The low ME content attained over Al_2O_3-supported CaO catalysts calcined at high temperatures was explained by the formation of less active phase of calcium aluminate [3]. Among the Ca-based three-component oxides investigated, CaMgZn and CaBaZn gave the high ME content, > 96% (Table 3). The results in Fig. 4 revealed that the initial rate of the transesterification over CaMgZn was higher. In the case of CaBaZn, the slow reaction rate in the first hour after which the yield of methyl esters rapidly increased suggested a change in the catalysis mechanism. Probably, the active phase leached at the initial stage of the reaction promoted the transesterification homogeneously. BaO possessed the solubility in methanol higher than CaO [8]. As shown in Table 3, CaBaZn exhibited a loss of Ca and Ba after being used.

Figure 5 shows the CO_2-TPD profiles of CaMgZn and CaBaZn oxides in comparison with that of pure $CaCO_3$ calcined at 800 °C. The peak appeared at 756 °C was assigned to BaO in CaBaZn. The desorption of CO_2 from MgO occurred at moderate temperatures (ca. 356 °C) whereas ZnO contributed to the weak basicity at temperatures < 200 °C. The peak related to CO_2 desorbed from CaO (678 °C) was shifted to lower temperatures when Ca formed the mixed oxides. The broad characteristics of the peaks should be ascribed to the presence of CaO clusters adjacent to other oxides. As summarized in Table 4, CaO derived from pure $CaCO_3$ possessed the highest basicity. However, the amount of basic sites determined by TPD of CO_2 does not always correlate with the catalytic performance since the adsorption of CO_2 with the small size is not selective. CaMgZn and CaBaZn had a similar relative basicity. The higher activity of CaMgZn should be attributed to the higher quantity of the sites with medium-to-strong basicity.

The effect of calcination temperatures on the transesterification over CaMgZn is shown in Fig. 6. The suitable temperature for the calcination was strongly linked with the temperature required for the decomposition of carbonate groups to generate the active oxides. The TGA result suggested the complete transformation of the carbonates into the oxides at temperatures > 700 °C (Fig. 3D). CaMgZn calcined at 800 °C yielded the highest ME content (Fig. 6). The decline in the amount of methyl esters produced, when the mixed precipitate was treated at 900 °C, should be due to a sintering of the active sites, similarly to the hard burn effect observed for the natural $CaMg(CO_3)_2$ [24].

CaBaZn exhibited a severe loss of the activity after being used twice (Fig. 7). Our previous study pointed out the polar organic molecules, including glycerol and glyceride derivatives, responsible for the deactivation of the mixed oxides due to a strong adsorption on the active oxides [11]. Kouzu et al. demonstrated the presence of calcium diglyceroxides as a product from the reaction of surface CaO with glycerol [25]. The formation of the glyceroxide species did not only hamper the conversion of triglycerides to the esters, but also resulted in the leaching of the active sites. The transesterification activity of both mixed oxides was restored after treating the spent catalysts with the solution of methanol and 5 M NH_4OH. Calcium diglycerides were hydrolysable in the presence of water [25]. The effective removal of the organic deposits was observed by the TGA analysis [11]. The lower ME content attained over CaBaZn after washing with the solution of methanol and 5 M NH_4OH should be related to a loss of active species by the leaching effect.

Conclusions

The Ca-based three-component oxides possessed low surface area due to the absence of intraparticle porosity. The XRD analysis indicated the formation of mixed carbonates of Ca and other divalent metal ions after which the corresponding oxides were generated. The co-precipitation of Ca with other metal ions resulted in the aggregation of small particles to bigger one in which the morphology depended on the types of metal ions. The TGA results revealed a large decrease in the decomposition temperature for $CaCO_3$, generating CaO, by the formation of CaMgZn mixed precipitate. CaMgZn exhibited a superior performance to CaBaZn and other three-component oxides studied due to the higher quantity of medium-to-strong basic sites. The calcination temperature of 800 °C was required for activating the CaMgZn precipitate to obtain the highest ME content. CaMgZn can be reused by which the suitable regeneration method was to wash with the solution of methanol and 5 M NH_4OH. The ongoing project is to investigate the effects of preparation conditions for CaMgZn, such as the concentration of Na_2CO_3 solution, the molar ratio of CO_3^{2-}/metal and the pH of synthesis mixture, on the methanolysis of palm kernel oil.

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Table 1

Methyl ester (ME) content obtained from transesterification[a] of PKO with methanol over various one-component oxides calcined at 800 °C for 2 h

Catalyst	ME content (wt.%)
MgO	3.0
CaO	46.2
BaO	0.3
ZnO	0.3
Al_2O_3	82.2

[a] Reaction conditions: catalyst amount, 10 wt.%; methanol/oil ratio, 30; temperature, 60 °C; time, 3 h.

Table 2

Elemental composition and physicochemical properties of two-component oxides

Catalyst (M_1M_2)	Na content[a] (wt.%)	Metal atomic ratio (M_1:M_2)			Particle size[d] (μm)	S_{BET}[e] (m^2 g^{-1})	ME content[f] (wt.%)
		Before the reaction		After the reaction			
		Mixture[b]	Precipitate[c]				
MgBa	1.84	1:1	1:3	1:2	1.1-6.4	4.2	17.6
MgZn	0.00		2:1	2:1	0.2-0.7	8.0	0.8
MgAl	33.40		2:1	3:1	0.1-0.4	60.0	96.5
BaZn	0.00		1:1	1:2	0.3-4.6	8.6	6.5
BaAl	2.27		1:1	1:2	*n.d.*[g]	9.6	10.7
ZnAl	21.15		3:1	2:1	0.3-0.6	51.6	94.4

[a] Na content in the precipitate determined by XRF spectroscopy.

[b] Atomic ratio of metals in the synthesis mixture.

[c] Atomic ratio of metals in the precipitate determined by XRF spectroscopy.

[d] Determined by SEM technique.

[e] BET surface area.

[f] Reaction conditions: methanol/oil molar ratio, 30; catalyst amount, 6 wt.%; reaction time, 3 h; temperature, 60 °C.

[g] Not determined.

Table 3

Elemental composition and physicochemical properties of Ca-based three-component oxides

Catalyst (CaM_1M_2)	Na content[a] (wt.%)	Metal atomic ratio ($Ca:M_1:M_2$)			Particle size[d] (μm)	CaO cluster size[e] (nm)	S_{BET}[f] ($m^2 g^{-1}$)	ME content[g] (wt.%)
		Before the reaction		After the reaction				
		Mixture[b]	Precipitate[c]					
CaMgBa	1.68	1:1:1	8:1:6	10:1:7	2.1-7.6	42.8	6.7	32.2
CaMgZn	0.00		2:1:3	2:1:3	0.2-0.5	22.7	9.2	96.4
CaMgAl	16.90		3:1:2	2:1:2	*n.d.*	38.9	10.3	40.5
CaBaZn	0.00		1:1:1	1:1:2	0.8-11.7	40.8	4.9	98.8
CaBaAl	3.65		1:2:1	1:2:1	*n.d.*	46.7	7.7	67.8
CaZnAl	0.00		1:2:1	*n.d.*[h]	0.2-0.8	30.4	11.4	12.0

[a] Na content in the precipitate determined by XRF spectroscopy.

[b] Atomic ratio of metals in the synthesis mixture.

[c] Atomic ratio of metals in the precipitate determined by XRF spectroscopy.

[d] Determined by SEM technique.

[e] Determined from XRD patterns using Sherrer's equation.

[f] BET surface area.

[g] Reaction conditions: methanol/oil molar ratio, 30; catalyst amount, 6 wt.%; reaction time, 3 h; temperature, 60 °C.

[h] Not determined.

Table 4

Relative basicity of various oxide catalysts determined by temperature-programmed desorption (TPD) of CO_2

Catalyst	Distribution of base sites[b]			Relative basicity[c]
	Weak	Medium	Strong	
CaO[a]	0.0	0.0	1.0	0.43
CaMgZn	0.04	0.24	0.72	0.30
CaBaZn	0.12	0.03	0.85	0.27

[a] Commercial $CaCO_3$ after calcination at 800 °C.

[b] Calculated from the profile area in the different ranges of temperatures: weak, 100–250 °C; medium, 250–500 °C; strong > 500 °C.

[c] Calculated from total area of the profiles.

Figure Captions

Fig. 1 SEM images of MgZn (A), CaMgZn (B), BaZn (C), CaBaZn (D), ZnAl (E) and CaZnAl (F) after the calcination at 800 ºC for 2 h.

Fig. 2 XRD patterns of mixed CaMgZn precipitates before (a) and after (b) the calcination at 800 ºC for 2 h. (Symbols: ▼ = $CaZn(CO_3)_2$, ⬟ = $CaMg(CO_3)_2$, ■ = $Zn(OH)_2$, ✦ = $Mg(OH)_2$, ▲ = $Ca(OH)_2$, ⬮ = CaO, ⧗ = MgO and ▰ = ZnO)

Fig. 3 TG and DTG curves of pure $CaCO_3$ (A) and mixed precipitates of CaMg (B), CaZn (C) and CaMgZn (D).

Fig. 4 Dependence of the ME content on time in the transesterification of palm kernel oil with methanol over CaMgZn (■) and CaBaZn (●). Reaction conditions: methanol/oil molar ratio, 30; catalyst amount, 6 wt.%; temperature, 60 °C.

Fig. 5 Profiles of temperature-programmed desorption of CO_2 for pure $CaCO_3$ (a), CaMgZn (b) and CaBaZn (c). Before the analysis, the samples were calcined at 800 ºC for 2 h.

Fig. 6 Effect of calcination temperatures for CaMgZn precipitate on the ME content in the transesterification of palm kernel oil with methanol. Reaction conditions: *see* Fig. 4.

Fig. 7 Reusability and regeneration of CaMgZn and CaBaZn. Reaction conditions: s*ee* Fig. 4.

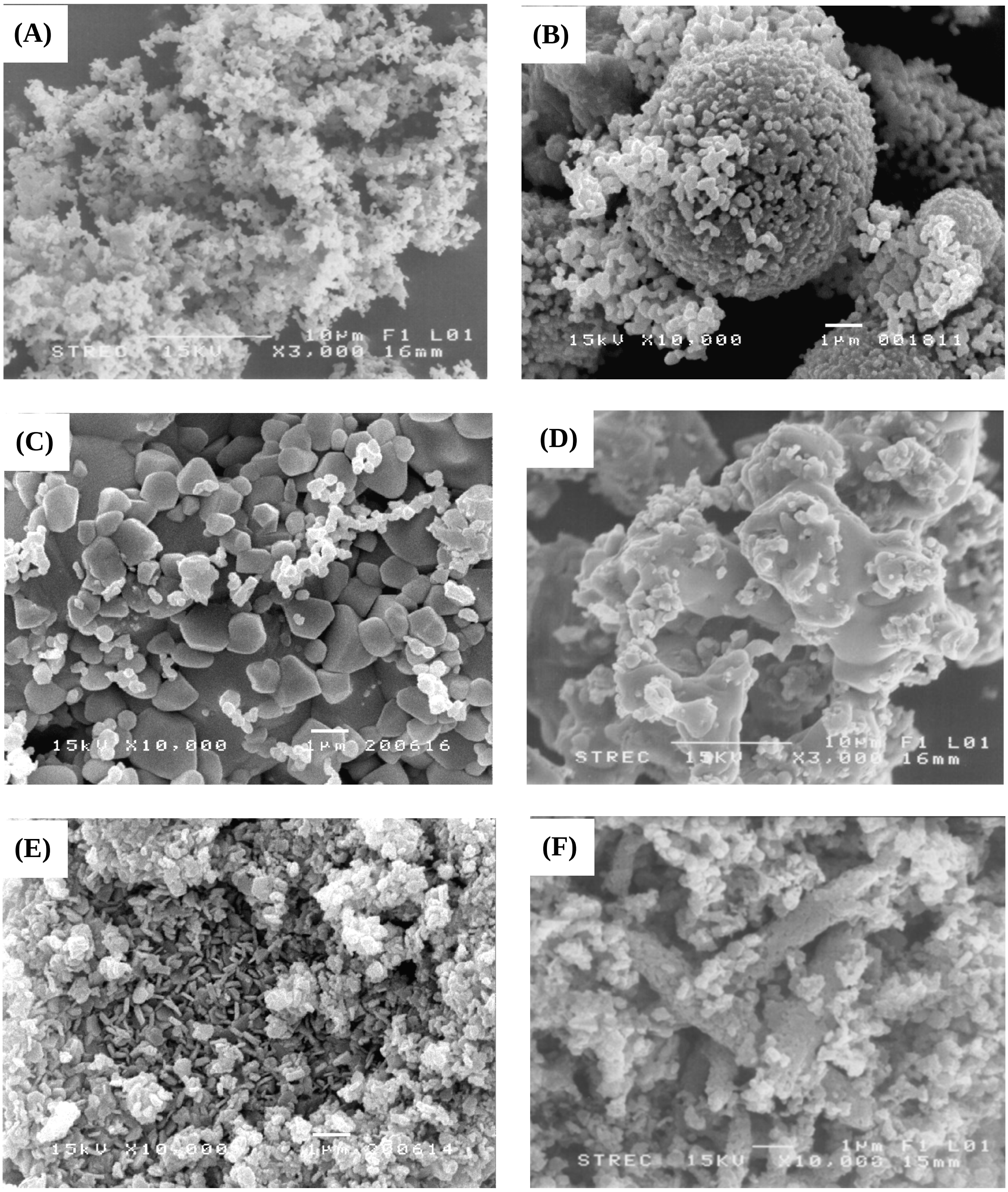
(A)
10μm F1 L01
STREC 15KV X3,000 16mm
(B)
15kV X10,000 1μm 001811
(C)
15kV X10,000 1μm 200616
(D)
10μm F1 L01
STREC 15KV X3,000 16mm
(E)
15kV X10,000 1μm 200614
(F)
1μm F1 L01
STREC 15KV X10,000 15mm

Fig. 1

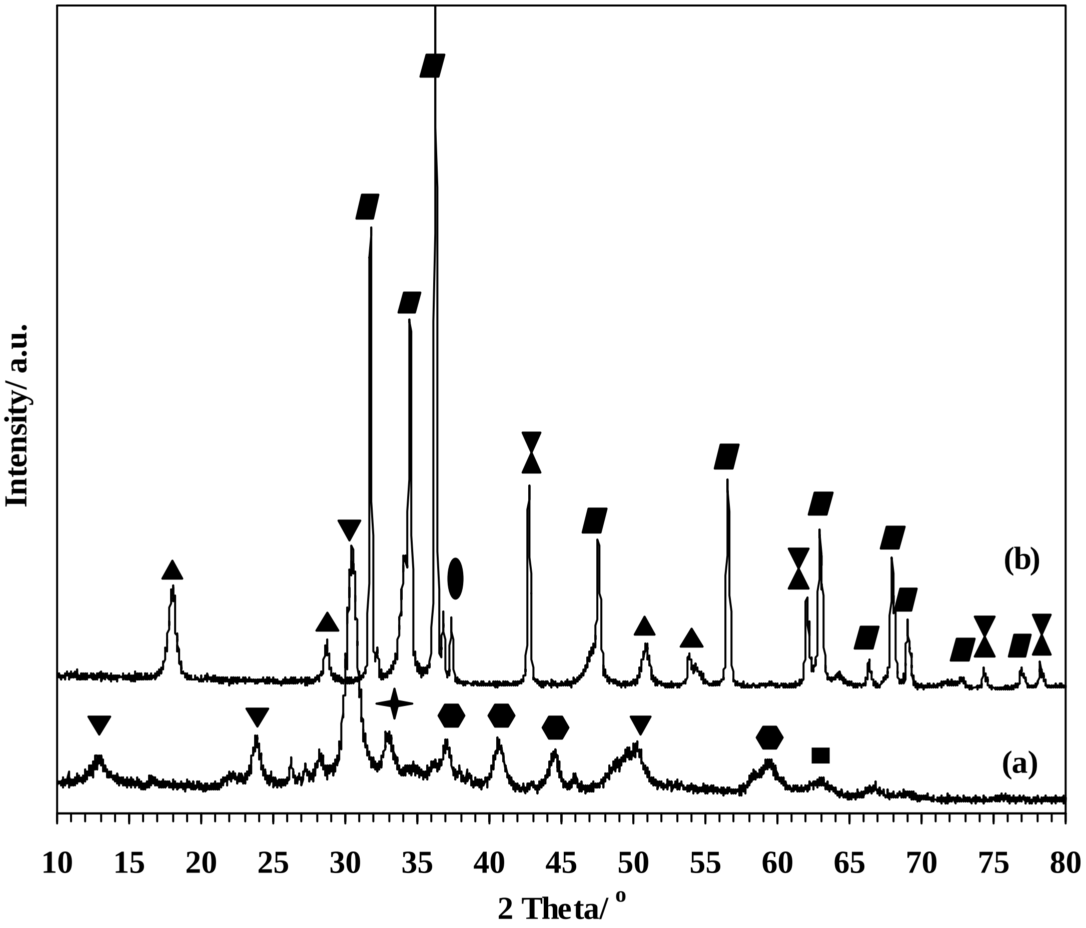

Fig. 2

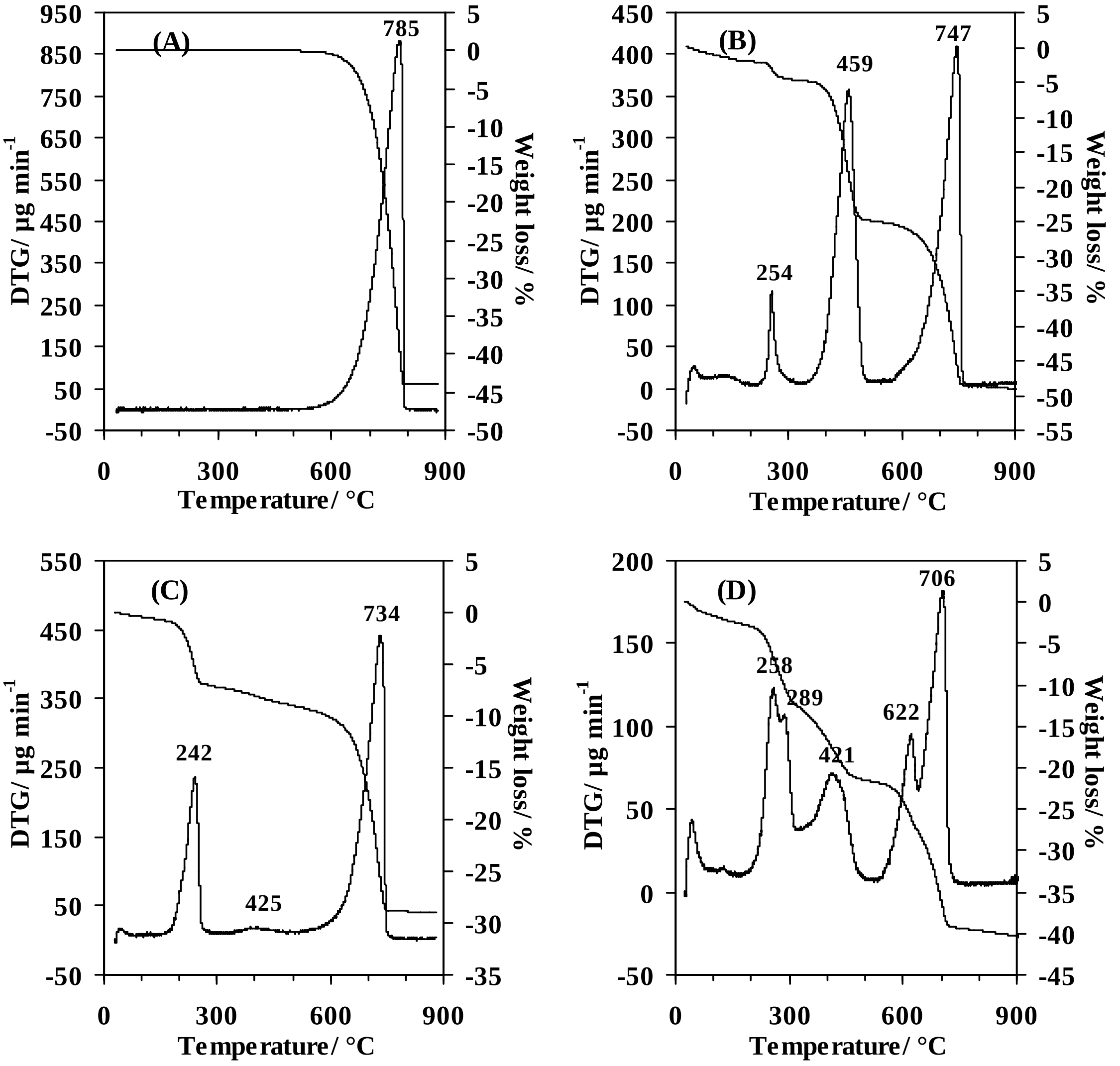
(A)
785
(B)
254
459
747
(C)
242
425
734
(D)
258
289
421
622
706
DTG/ µg min^{-1}
Weight loss/ %
Temperature/ °C
0
300
600
900
950
850
750
650
550
450
350
250
150
50
-50
400
350
300
250
200
150
100
50
0
500
450
350
250
150
50
200
150
100
50
0
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55

Fig. 3

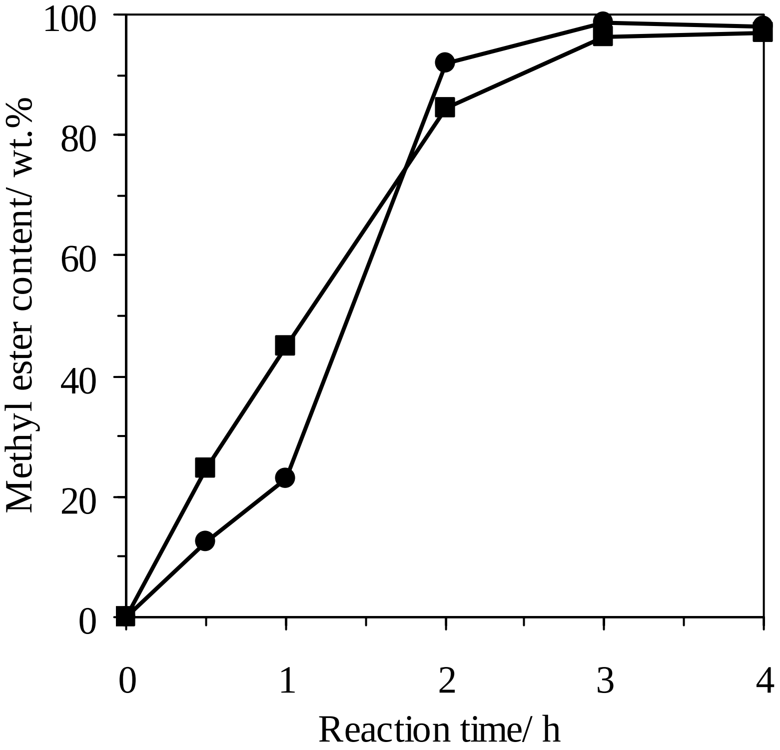
Methyl ester content/ wt.%
100
80
60
40
20
0
0
1
2
3
4
Reaction time/ h

Fig. 4

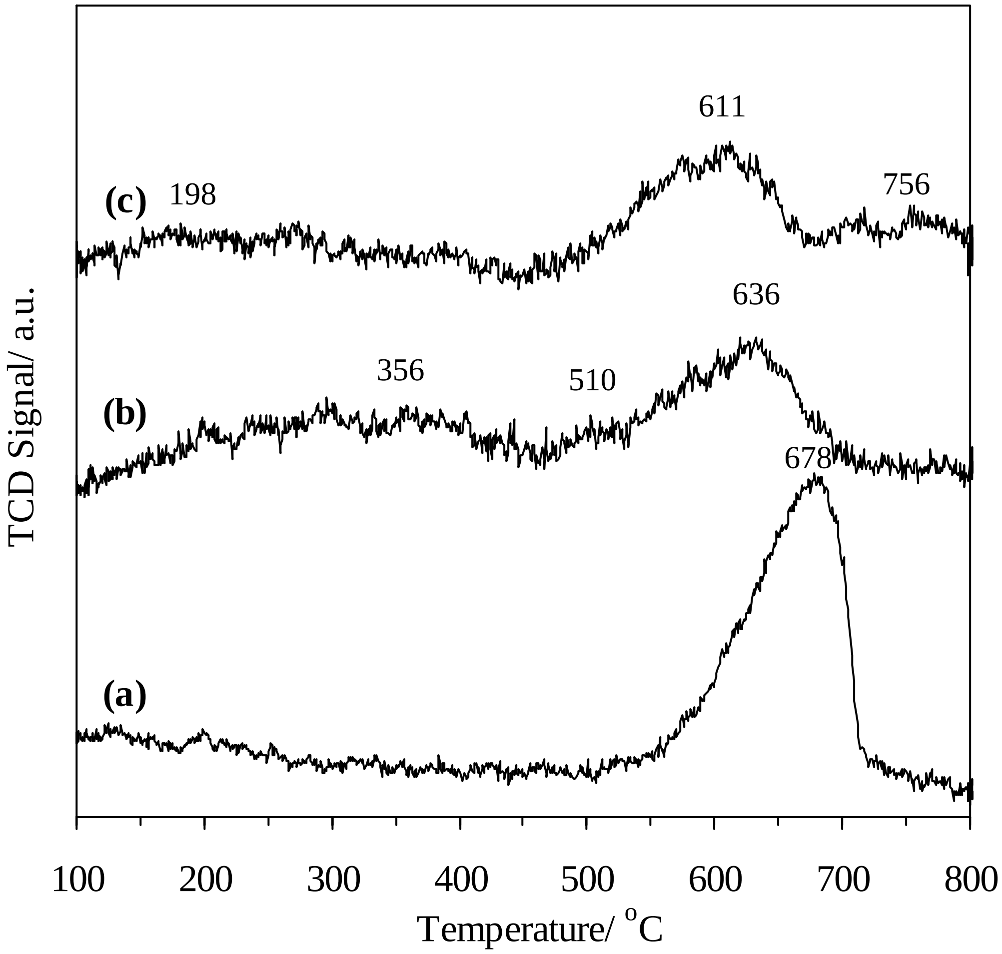
611
(c)
198
756
636
356
510
(b)
678
(a)
TCD Signal/ a.u.
100
200
300
400
500
600
700
800
Temperature/ °C

Fig. 5

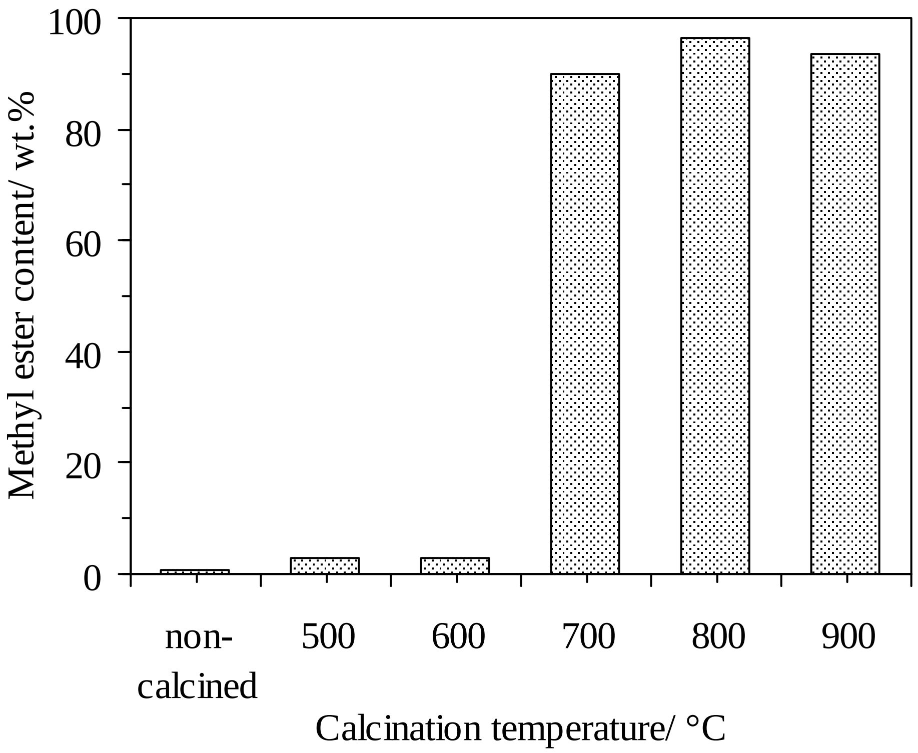
100
80
60
40
20
0
Methyl ester content/ wt.%
non-calcined
500
600
700
800
900
Calcination temperature/ °C

Fig. 6

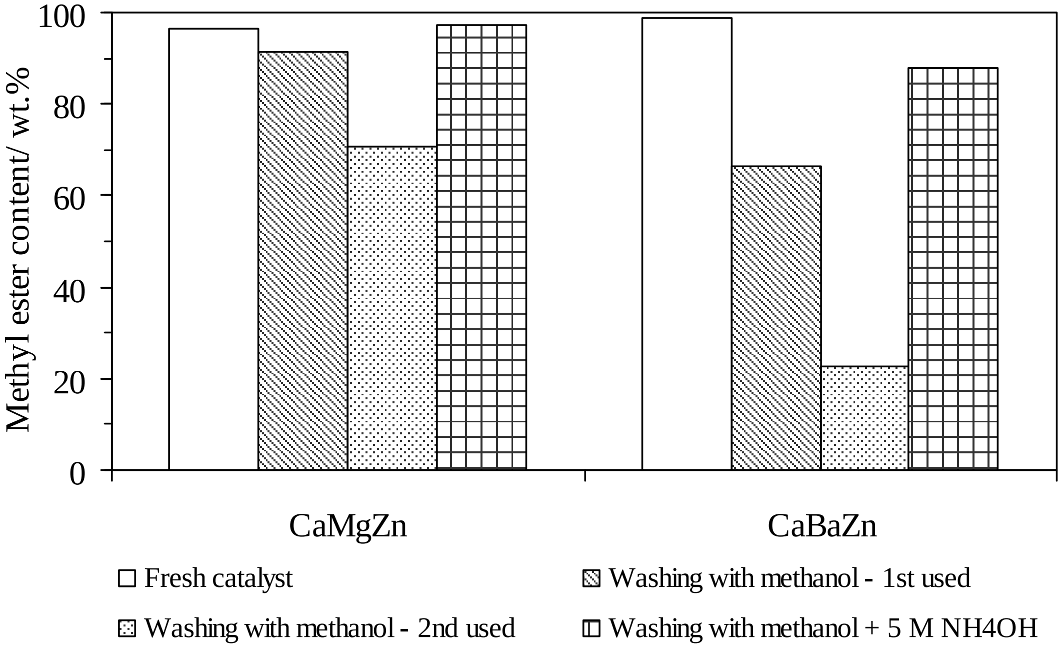
Methyl ester content/ wt.%
0
20
40
60
80
100
CaMgZn
CaBaZn
☐ Fresh catalyst
▧ Washing with methanol - 1st used
▨ Washing with methanol - 2nd used
⊞ Washing with methanol + 5 M NH4OH

Fig. 7