รายงานวิจัยฉบับสมบูรณ์

โครงการ

การศึกษาการปรับปรุงลักษณะสมบัติของโลหะออกไซด์ผสมสำหรับปฏิกิริยาทรานส์เอสเทอริฟิเคชันที่ถูกเร่งแบบวิวิธพันธ์

โดย

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จุฬาลงกรณ์มหาวิทยาลัย

มิถุนายน 2551

สัญญาเลขที่ MRG4980112

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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

บทคัดย่อ

รหัสโครงการ : MRG4980112

ชื่อโครงการ : การศึกษาการปรับปรุงลักษณะสมบัติของโลหะออกไซด์ผสมสำหรับปฏิกิริยาทรานส์เอสเทอริฟิเคชันที่ถูกเร่งแบบวิวิธพันธ์

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โครงการวิจัยนี้ศึกษาการเตรียมและการวิเคราะห์ลักษณะสมบัติของโลหะออกไซด์ผสมสำหรับเร่งปฏิกิริยาทรานส์เอสเทอริฟิเคชันของน้ำมันเมล็ดในปาล์มกับเมทานอลที่อุณหภูมิ 60 องศาเซลเซียสและความดัน 1 บรรยากาศ โลหะออกไซด์ผสมเตรียมขึ้นโดยวิธีตกตะกอนร่วมสารละลายเกลือไนเตรตผสมของโลหะสองชนิดเลือกจาก Ca, Mg, Ba, Zn, Al และ La กับสารละลายเกลือคาร์บอเนตที่อุณหภูมิห้องและภาวะเป็นกลาง การวิเคราะห์ตัวเร่งปฏิกิริยาด้วยเทคนิค XRD, SEM, N_2 adsorption-desorption measurement และ TGA แสดงให้เห็นว่า โลหะออกไซด์ผสมมีขนาดอนุภาคเล็กกว่าและพื้นที่ผิวสูงกว่าออกไซด์ของโลหะองค์ประกอบเดียว ซึ่งช่วยลดอุณหภูมิในการเผาเพื่อเปลี่ยนโลหะคาร์บอเนตเป็นโลหะออกไซด์ที่ว่องไวในปฏิกิริยา CaZn เป็นตัวเร่งปฏิกิริยาสององค์ประกอบที่ว่องไวที่สุด จากการศึกษาผลของอัตราส่วนโดยโมลของ Ca/Zn ในตัวเร่งปฏิกิริยาออกไซด์ผสม ปริมาณตัวเร่งปฏิกิริยา อัตราส่วนโดยโมลของเมทานอล/น้ำมัน เวลาในการทำปฏิกิริยา และปริมาณน้ำที่มีต่อผลได้ของเมทิลเอสเทอร์ พบว่าที่ภาวะที่เหมาะสมคือ ปริมาณตัวเร่งปฏิกิริยาเท่ากับร้อยละ 10 อัตราส่วนโดยโมลของเมทานอล/น้ำมันเท่ากับ 30 เวลาในการทำปฏิกิริยาเท่ากับ 1 ชั่วโมง ตัวเร่งปฏิกิริยา CaZn ที่มีอัตราส่วนโดยโมลของ Ca/Zn เท่ากับ 0.25 จะได้ร้อยละเมทิลเอสเทอร์สูงสุดเท่ากับ 94 ตัวเร่งปฏิกิริยานี้ยังสามารถใช้เร่งปฏิกิริยาทรานส์เอสเทอริฟิเคชันของน้ำมันปาล์มโอเลอิน น้ำมันถั่วเหลือง และน้ำมันดอกทานตะวันได้ นอกจากนี้ยังศึกษาผลของวิธีการฟื้นฟูสภาพตัวเร่งปฏิกิริยาต่อการนำตัวเร่งปฏิกิริยากลับมาใช้ใหม่ด้วย

คำหลัก : ไบโอดีเซล ทรานส์เอสเทอริฟิเคชัน ตัวเร่งปฏิกิริยาวิวิธพันธุ์ โลหะออกไซด์ผสม

ABSTRACT

Project Code : MRG4980112

Project Title : Study of Characteristic Modifications of Mixed Metal Oxides for Heterogeneously Catalyzed Transesterification

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Preparation and characterization of mixed metal oxides for transesterification of palm kernel oil with methanol at 60 °C and 1 atm have been studied. Mixed metal oxides were prepared via a conventional co-precipitation of mixed nitrate solution of two metals selected from Ca, Mg, Ba, Zn, Al and La in the presence of a soluble carbonate salt at near neutral conditions. Characterizations by techniques of XRD, SEM, N_2 adsorption-desorption measurement and TGA indicated that the mixed oxides possess relatively small particle sizes and high surface areas, compared to one-component oxides, resulting in a reduction of the calcination temperature required for conversion of metal carbonate precipitates to active oxides. CaZn is the most active two-component catalyst. Influences of Ca/Zn atomic ratio in the mixed oxide catalyst, catalyst amount, methanol/oil molar ratio, reaction time, and water amount on the methyl ester (ME) content were studied. Under the suitable transesterification conditions at 60 °C (catalyst amount = 10 wt.%, methanol/oil molar ratio = 30, reaction time = 1 h), the ME content of > 94 % can be achieved over CaZn catalyst with the Ca/Zn ratio of 0.25. The mixed oxide can be also applied to transesterification of palm olein, soybean, and sunflower oils. Furthermore, the effects of different regeneration methods on the reusability of CaZn catalyst were investigated.

Keywords : Biodiesel, Transesterification, Heterogeneous catalyst, Mixed metal oxide

สรุปย่อ
EXECUTIVE SUMMARY

ในการดำเนินโครงการเป็นระยะเวลา 2 ปี ผู้วิจัยได้ศึกษาการเตรียมและการวิเคราะห์ลักษณะสมบัติของโลหะออกไซด์ผสมสององค์ประกอบ สำหรับใช้เป็นตัวเร่งปฏิกิริยาในทรานส์เอสเทอริฟิเคชันของน้ำมันเมล็ดในปาล์มกับเมทานอลเพื่อผลิตไบโอดีเซล โดยมีเป้าหมายพัฒนาตัวเร่งปฏิกิริยาโลหะออกไซด์ผสมที่มีความว่องไวสูงด้วยวิธีการตกตะกอนร่วม (co-precipitation) ศึกษาหาภาวะที่เหมาะสมในการเตรียม ได้แก่ ชนิดและอัตราส่วนโลหะ ความเป็นกรด-เบส (pH) สารตกตะกอน (precipitant) อุณหภูมิการเผา (calcination) เป็นต้น จากนั้นทดสอบความว่องไวของโลหะออกไซด์ผสมที่เตรียมได้ ในการเร่งปฏิกิริยาทรานส์เอสเทอริฟิเคชันของน้ำมันเมล็ดในปาล์มและเมทานอลที่อุณหภูมิ 60 องศาเซลเซียส และความดัน 1 บรรยากาศ โดยใช้ชุดทดลองปฏิกิริยาขนาด 250 มิลลิลิตร และศึกษาผลของอัตราส่วนโดยโมลของเมทานอลต่อน้ำมัน ปริมาณตัวเร่งปฏิกิริยา และเวลาในการทำปฏิกิริยาต่อร้อยละความบริสุทธิ์และร้อยละผลได้เมทิลเอสเทอร์ เพื่อให้ได้ภาวะที่เหมาะสมในการผลิตไบโอดีเซล และทำการวิเคราะห์ลักษณะสมบัติของโลหะออกไซด์ผสมที่เตรียมได้ด้วยเทคนิคต่าง ๆ เพื่ออธิบายผลของปฏิกิริยา และเป็นองค์ความรู้ต่อยอดงานวิจัยที่จะดำเนินต่อไป

ตัวเร่งปฏิกิริยาที่เตรียมได้เป็นโลหะออกไซด์ผสมแบบสององค์ประกอบของ Mg, Ca, Ba, Zn, Al และ La จากการทดสอบความว่องไวเบื้องต้น (preliminary screening) ในการเร่งปฏิกิริยาทรานส์เอสเทอริฟิเคชันของน้ำมันเมล็ดในปาล์มกับเมทานอลที่อุณหภูมิ 60 องศาเซลเซียส พบว่า ออกไซด์ผสมแบบสององค์ประกอบของ MgAl, MgZn, CaBa, CaZn, CaLa, ZnAl และ ZnLa ให้ร้อยละเมทิลเอสเทอร์มากกว่า 90 ที่อัตราส่วนโดยโมลเมทานอลต่อน้ำมัน 30-70 ปริมาณตัวเร่งปฏิกิริยาร้อยละ 10 เทียบกับน้ำหนักน้ำมันที่ใช้ โดยที่ CaZn เป็นออกไซด์ผสมที่มีความว่องไวในการเร่งปฏิกิริยามากที่สุด

จากนั้นนำตัวเร่งปฏิกิริยา CaZn มาศึกษาหาภาวะที่เหมาะสมในการเตรียม โดยพบว่าอัตราส่วนโดยโมลของ Ca/Zn ที่เหมาะสมคือ 0.25 (CaZn-0.25) สารตกตะกอนที่เหมาะสมคือ Na_2CO_3 ความเป็นกรด-เบสเท่ากับ 7 และอุณหภูมิในการเผา 800 องศาเซลเซียส เป็นเวลา 2 ชั่วโมง และเมื่อนำตัวเร่งปฏิกิริยา CaZn ที่ได้จากภาวะการเตรียมที่เหมาะสม ไปศึกษาหาภาวะที่เหมาะสมในการเร่งปฏิกิริยาทรานส์เอสเทอริฟิเคชันของน้ำมันเมล็ดในปาล์มกับเมทานอล ที่อุณหภูมิ 60 องศาเซลเซียส พบว่า ภาวะที่เหมาะสมคือ อัตราส่วนโดยโมลของเมทานอลต่อน้ำมันเป็น 30 ปริมาณตัวเร่งปฏิกิริยาร้อยละ 10 โดยน้ำหนัก (เทียบกับน้ำหนักของน้ำมันที่ใช้) เวลาในการทำปฏิกิริยา 1 ชั่วโมง ได้ร้อยละเมทิลเอสเทอร์เท่ากับ 94.8

ตัวเร่งปฏิกิริยา CaZn-0.25 สามารถใช้เร่งทรานส์เอสเทอริฟิเคชันของน้ำมันพืชชนิดอื่น ๆ ได้แก่ น้ำมันปาล์มโอเลอิน น้ำมันถั่วเหลือง และน้ำมันดอกทานตะวัน โดยให้ร้อยละเมทิลเอสเทอร์มากกว่า 90 นอกจากนั้นในโครงการนี้ยังได้ศึกษาหาวิธีที่เหมาะสมในการฟื้นฟูสภาพตัวเร่งปฏิกิริยา (catalyst regeneration) และการนำตัวเร่งปฏิกิริยากลับมาใช้ใหม่ (reusability) โดยเปรียบเทียบวิธีการฟื้นฟูสภาพด้วยความร้อน (thermal treatment) และการล้างด้วยตัวทำละลาย (solvent washing) พบว่า การล้างตัวเร่งปฏิกิริยาที่ใช้แล้วด้วยสารละลายผสมของเมทานอลกับ NH_4OH ความเข้มข้น 0.5 โมลาร์ เป็นวิธีที่ดีที่สุด และตัวเร่งปฏิกิริยาสามารถนำกลับมาใช้ใหม่ได้อย่างน้อย 3 ครั้ง โดยให้ร้อยละเมทิลเอสเทอร์มากกว่า 90

เมื่อนำตัวเร่งปฏิกิริยาโลหะออกไซด์ผสม CaZn ไปวิเคราะห์ลักษณะสมบัติด้วยเทคนิคต่าง ๆ ได้แก่ powder X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray fluorescence spectroscopy (XRF), thermogravimetric analysis (TGA) และ N_2 adsorption-desorption measurement พบว่า Ca เป็นตำแหน่งเบสที่ว่องไว (active base site) ในการเร่งปฏิกิริยา การเกิดเป็นโลหะออกไซด์ผสมทำให้ขนาดอนุภาคของตัวเร่งปฏิกิริยาที่ได้ลดลง โดยที่ CaZn-0.25 มีขนาดอนุภาคเฉลี่ยเท่ากับ 1 ไมครอน นอกจากนั้น ทำให้พื้นที่ผิวเพิ่มขึ้น (52 ตารางเมตร/กรัม) ซึ่งช่วยลดอุณหภูมิในการเผาเพื่อเปลี่ยนโลหะคาร์บอเนตเป็นโลหะออกไซด์ที่ว่องไวในปฏิกิริยา เมื่อนำตัวเร่งปฏิกิริยา CaZn-0.25 ก่อนและหลังการใช้ในปฏิกิริยาไปวิเคราะห์หาองค์ประกอบธาตุ พบว่า เกิดการหลุดของ Ca และ Zn น้อยมาก จึงน่าจะเป็นตัวเร่งปฏิกิริยาที่มีศักยภาพพัฒนาต่อไปเพื่อใช้ในกระบวนการผลิตระดับที่ใหญ่ขึ้นได้

เนื้อหางานวิจัย

1. Introduction

Biodiesel, a mixture of alkyl esters, is an alternative biomass-based fuel derived from vegetable oils and animal fats. Since its physicochemical and fuel properties are similar to those of petroleum-based diesel oil, biodiesel can be applied to compression-ignition diesel engines with little or no modifications. A long with non-toxicity and biodegradability, exhaust gas from biodiesel combustion contains no SO_x and relatively small amounts of CO, unburnt hydrocarbons, and particulate matter when compared to the combustion products of conventional diesel fuel [1-4].

In a conventional process for biodiesel production, triglycerides in oils and fats are converted to alkyl esters by transesterifying with small alcohols in the presence of base at 60-100 ºC [5-8]. Although the reaction itself is easily performed, subsequent neutralization, separation, and purification steps are time-consuming and non-environmentally friendly due to a requirement of several washing stages that use a large amount of water [2]. Consequently, a considerable amount of highly caustic wastewater is inevitably produced. These drawbacks significantly contribute additional cost to the final biodiesel product. Replacement of the homogeneous catalysis with a heterogeneous route has received much attention since the process can be simplified by facilitating the catalyst separation and purification steps [9]. Recently, the French Institute of Petroleum (IFP) has commercialized the first heterogeneously catalyzed biodiesel production process at Sète, using a spinel mixed oxide of Zn and Al as a solid base catalyst [9,10]. However, it seems that the reaction requires high temperature and high pressure conditions, probably due to relatively low basicity and activity of the catalyst.

Al_2O_3-supported alkali metal oxide catalysts [11-14], for example Na/NaOH/γ-Al_2O_3 [11] and K_2CO_3/Al_2O_3 [12], are highly basic and are very active in the transesterification of vegetable oils. However, the active oxide components are sensitive to moisture and are easily leached by methanol [15], limiting their industrial application. Suppes et al. revealed that the rapeseed oil conversion of > 95 % can be achieved by using natural $CaCO_3$ rock when the reaction was carried out at ca. 200 °C [16]. CaO is a more active catalyst and has been widely investigated in the transesterification studies

[17-23]. Despite its low cost and availability, CaO possesses high basic strength (H_- = 26.5) [23] and low solubility in methanol [17]. Compared to pure CaO, the combination of CaO and MgO gave higher alkyl ester yield [18]. The enhancement of alkyl ester formation may occur via a bifunctional catalysis route.

Commercially, CaO is produced via a thermal decomposition of high-purity limestone calcite ($CaCO_3$) at temperatures higher than 825 °C [24]. The temperatures as high as 1038-1343 ºC were reported [24]. When the calcination was performed at 800 ºC, the resulting mixed oxide of Ca and Mg derived from dolomite, a natural mixed carbonate rock ($CaMg(CO_3)_2$), exhibited superior activity to the calcined calcite [25]. It was suggested by XRD that, at this calcination temperature, dolomite has higher amounts of active CaO. The result is related to the fact that dolomite is transformed to the corresponding active mixed oxides at relatively low temperatures via dual-stage decomposition [24].

ZnO with weakly hydrogenating character also possesses basic properties [26]. Similarly to the case of CaO, the transesterification activity of ZnO catalyst can be improved by impregnation of a Zn precursor on MgO support [18]. This result emphasizes the advantage of co-existence of two different basic-oxide components in the catalyst for transesterification. To our best knowledge, no study on catalytic performance of CaZn mixed oxide in the transesterification of vegetable oils has been reported. Ngamcharussrivichai et al. revealed that CaO generated from decarbonation of $CaCO_3$ is more active in the transesterification of palm kernel oil than that derived from $Ca(OH)_2$ precipitate [27]. Therefore, we have prepared our CaZn catalysts via co-precipitation method using carbonates of sodium or ammonium as a precipitant. Physicochemical properties of the mixed oxide catalysts were studied by using various characterization techniques. The influences of conditions for mixed oxide preparation, vegetable oil transesterification, and catalyst regeneration on the methyl ester (ME) content have also been investigated.

2. Objectives

1. To prepare active CaZn mixed oxide for transesterification of palm kernel oil with methanol.
2. To characterize physico-chemical properties of CaZn mixed oxide catalysts by various techniques.

3. To find suitable conditions for transesterification of palm kernel oil with methanol using CaZn mixed oxide as a heterogeneous base catalyst.

3. Experimental

3.1 Catalyst Preparation

A mixed oxide of Ca and Zn was prepared according to the conventional co-precipitation of a mixed aqueous solution of $Ca(NO_3)_2{\cdot}4H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ (AR grade, Ajax Finechem). Na_2CO_3 or $(NH_4)_2CO_3$ (AR grade, Ajax Finechem) was used as a precipitant. For a typical catalyst preparation, required amounts of $Ca(NO_3)_2{\cdot}4H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ were completely dissolved in deioized water and then an aqueous solution of carbonate salt was slowly added under vigorous stirring at ambient temperature. The pH of the solution was maintained between 7 and 8. When $(NH_4)_2CO_3$ was used as the precipitant, the pH was controlled by adding an NH_4OH solution. The resulting mixture was then aged overnight (~20 h) at 60 °C. Moreover, urea hydrolysis method [28] was adapted in the present study. After carefully stirring the mixed metal nitrate solution with a urea solution at room temperature, we loaded the mixture (pH = 8-9) in a Teflon-lined autoclave and hydrothermally treated it at 110 °C for 24 h. The solid product was recovered by filtration, followed by thorough washing with deionized water and drying in an oven at 120 °C overnight. Before being applied as a catalyst, the dried solid was calcined in a muffle furnace at temperatures of 600-900 °C for 2-6 h. Hereafter, the mixed oxide catalyst was designated as CaO·ZnO-*X*, where *X* represents the Ca/Zn atomic ratio.

3.2 Characterization

Oxide structure and cluster size of the synthesized CaO·ZnO were determined by techniques of powder X-ray diffraction (XRD) using a Rigaku DMAX 2200/Ultima+ diffractometer equipped with Cu Kα radiation. Elemental analysis was performed on an ED-2000 energy dispersive X-ray fluorescence (XRF) spectrometer. Morphological study was carried out with a 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 $^{\circ}C\ min^{-1}$ under dry air flow. BET surface area and textural properties of mixed oxides were measured by techniques of N_2 physisorption using a Micromeritic ASAP 2020 surface area and porosity analyzer.

3.3 Transesterification Procedure

Refined palm kernel oil (PKO) was donated by Chumporn Palm Oil Industry Co., Ltd. Refined sunflower oil, palm olein oil, and soybean oil are typical edible cooking oil purchased from a supermarket. Methanol was commercial grade with 99.5 % purity. These liquids were used without further purification. Transesterification was carried out in a 150-mL 3-neck round bottom flask equipped with a reflux condenser and a magnetic stirrer. Typically, 1 g of calcined CaO·ZnO was suspended in a required volume of methanol. The temperature of the mixture was controlled at 60 °C by a water bath. Subsequently, oil was added into the mixture under vigorous stirring. The methanol/oil molar ratio was varied between 10 and 70. After the course of reaction (0.5-3 h), the catalyst was separated by centrifuge and the reaction mixture was then loaded into a rotary evaporator to remove excess methanol. Methyl ester phase was recovered in a separating funnel, followed by washing with deionized water and drying with Na_2SO_4.

Products in the methyl ester phase consist of methyl esters, monoglycerides, diglycerides, and unreacted triglycerides. Composition of the methyl esters was analyzed with a Varian CP-3800 gas chromatograph (GC) equipped with a FID detector and a 30-m DB-1 capillary column. The amounts of methyl esters produced were calculated based on an internal standard method using methyl undecanoate as a reference standard. Methyl ester (ME) content is defined as follows:

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

4. Results and Discussion

4.1 Characterization of CaZn Catalysts

Elemental composition and physicochemical properties of synthesized oxide catalysts are summarized in Table 1. It can be seen that the Ca/Zn atomic ratios of mixed oxides obtained in the presence of Na_2CO_3 were lower than those intended. The difference was more pronounced when the desired ratio of mixed oxide was increased. This result is consistent with the fact that Ca^{2+} is favorably precipitated at pH values higher than the pH of synthesis mixture, while Zn precipitate is formed more readily at this condition [29]. Under the present preparation conditions, Zn^{2+} should be precipitated much faster than Ca^{2+}. In addition, the elemental analysis indicated that there was no detectable amount of Na^{+} remaining in the CaZn precipitates after the calcination. For

other known mixed oxides prepared via the co-precipitation with Na_2CO_3, some specific structures, e.g. layered double hydroxides [30] and sodium dawsonite [31], are attained, where Na^+ plays an important role as a surface-charge balance cation. Unlikely, no additional oxide structures were found in the final CaZn catalyst as suggested by the XRD analysis (not shown here). The XRD patterns of Ca-Zn precipitates calcined at 800 °C revealed only diffraction peaks corresponding to CaO and ZnO with Wurzite structure, both of which are similar to those of calcined pure CaO and ZnO, respectively. Therefore, it is likely that the mixed oxides of Ca and Zn do not form any specific structures but they are present as separate oxide clusters in the precipitate particles.

Table 1 Elemental composition and physicochemical properties of calcined CaZn catalysts with different Ca/Zn ratios

Catalyst	Ca/Zn atomic ratio		Particle size[c] (μm)	Cluster size[d] (nm)		S_{BET}[e] ($m^2\ g^{-1}$)	V_{ave}[f] ($cm^3\ g^{-1}$)	D_{ave}[g] (Å)
	Mixture[a]	Solid[b]		CaO	ZnO			
CaO	∞	*n.d.*[h]	2.1-7.6	*n.d.*	*n.d.*	13.8	0.10	214.8
ZnO	0	*n.d.*	0.2-0.4	*n.d.*	*n.d.*	69.4	0.15	77.9
CaZn	0.25	0.23	0.2-1.2	41.4	36.8	52.8	0.12	84.6
	0.67	0.53	*n.d.*	59.0	56.4	52.0	0.11	87.6
	1	0.83	0.2-4.4	74.6	64.0	33.4	0.07	91.3
	1.5	1.14	*n.d.*	81.1	61.9	23.2	0.07	99.1
	4	2.32	0.2-9.7	93.0	58.1	16.6	0.05	125.3

[a] Ca/Zn atomic ratio in the synthesis mixture.

[b] Ca/Zn atomic ratio in the final catalyst determined by XRF spectroscopy.

[c] Determined by SEM technique.

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

[e] BET surface area.

[f] Average pore volume.

[g] Average pore diameter.

[h] Not determined.

The nano-sizes of CaO and ZnO clusters shown in Table 1 were estimated from the XRD patterns using Sherrer's equation [32]. When the Ca/Zn atomic ratio was increased, the size of both oxide clusters increased. This result is consistent with the results obtained from morphological studies by SEM technique (Fig. 1). Calcined pure Ca precipitate exhibited rough surface particles with diameters of 2.1-7.6 μm (Fig. 1A). For incorporation of Zn up to the Ca/Zn ratio between 1 and 4, two types of oxide particles were present (Fig. 1B-D). The small round-shape particles with average diameter of 1 μm were similar to those of pure ZnO (Fig. 1F). The other type exhibited

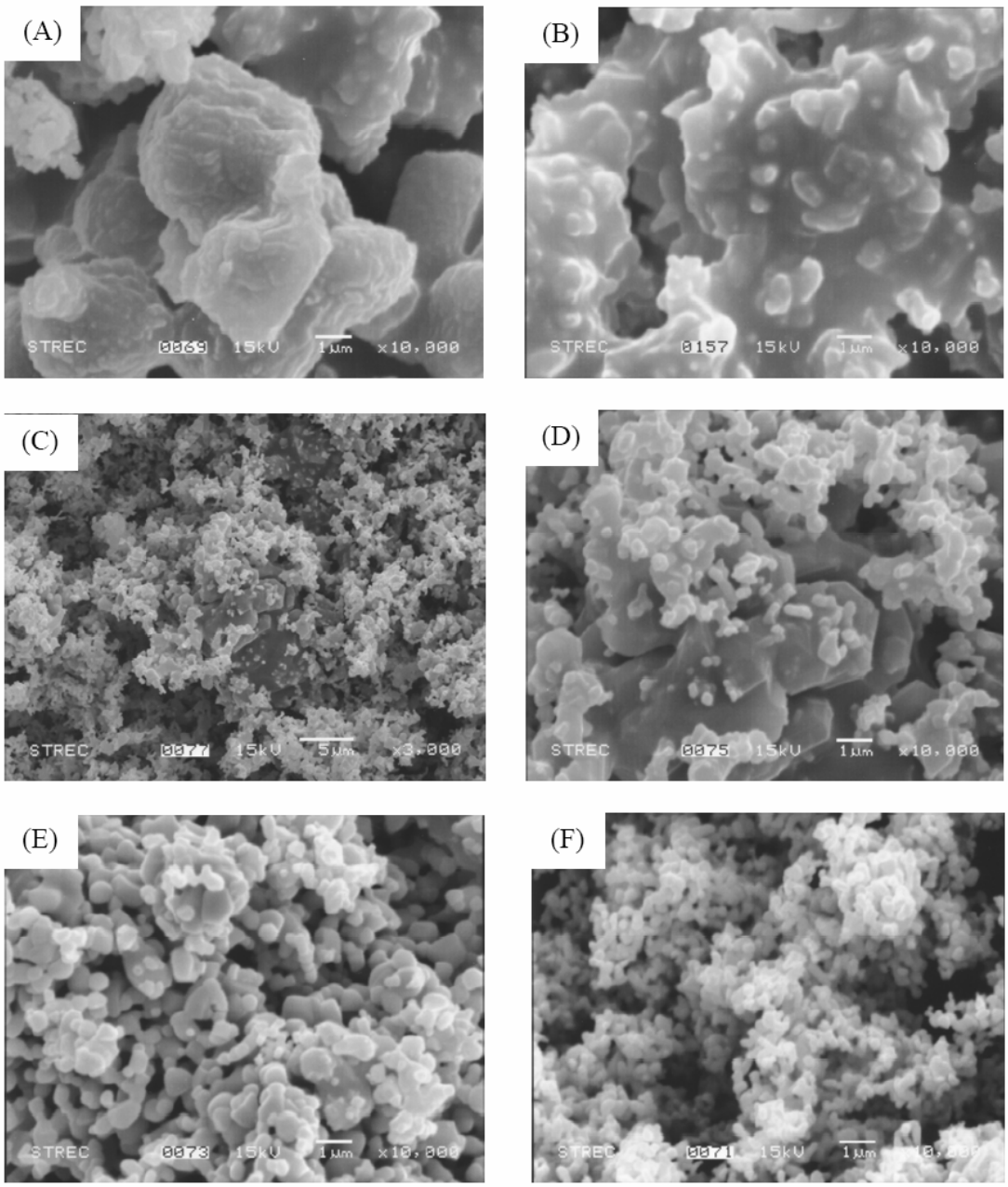


Fig. 1 SEM images of pure Ca precipitate (A), CaZn precipitates with the Ca/Zn atomic ratios of 4.0 (B), 1.0 (C and D (× 10,000)), and 0.25 (E), and pure Zn precipitate (F) after the calcination at 800 °C.

large particles with the shape and size close to those of pure CaO (Fig. 1A). One may deduce from these results that the smaller one includes mainly ZnO, while the larger one consists of CaO as the major component.

At the ratio of 4, the small particles were merged together and became embedded in the large ones (Fig. 1B). With the presence of Ca^{2+} as the major metal component in the synthesis solution, the previously formed Zn precipitate clusters can be covered by Ca carbonate subsequently precipitated during aging. The separation of two morphologies was evident when the amount of Ca was decreased to the Ca/Zn

ratios in the range of 0.67-1. The homogeneous form of round shape particles with diameter of 0.2-1.2 μm was obtained at the ratio of 0.25 (Fig. 1E). Increasing the amount of Zn or decreasing the Ca/Zn ratio not only resulted in the uniform morphology and small particle size, but also enhanced BET surface area and average pore volume (Table 1).

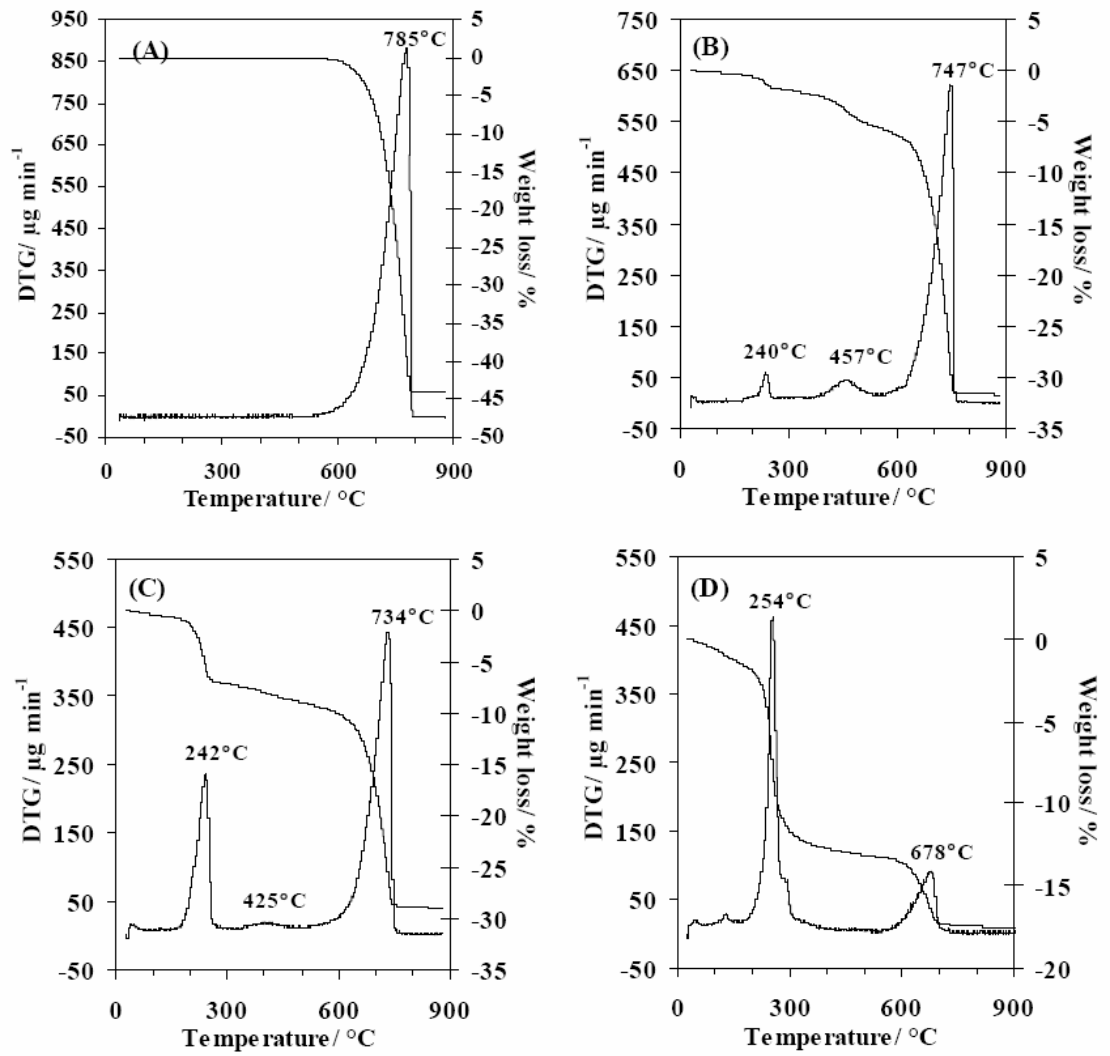


Fig. 2 Weight loss and DTG curves of non-calcined pure Ca precipitate (A) and CaZn precipitates with the Ca/Zn atomic ratios of 4.0 (B), 1.0 (C), and 0.25 (D).

Figure 2 shows thermal decomposition patterns of CaZn precipitates with different Ca/Zn ratios. Pure Ca precipitate exhibited one-step decomposition at 785 °C (Fig. 2A), corresponding to 44.3 wt.% of CO_2 released from $CaCO_3$ (theoretically 44.0 wt.%), while pure Zn precipitate showed the major weight loss at 237 °C with the extent of decomposition to 600 °C (not shown here), similarly to basic Zn carbonates reported earlier [33]. It can be seen that the peak corresponding to $CaCO_3$ decomposition was shifted to lower temperatures concomitantly with a reduction of total weight loss on

increasing the amount of Zn or decreasing the Ca/Zn ratio in the mixed precipitates (Fig. 2B-D). This result suggests that the incorporation of Zn decreases the temperature required for $CaCO_3$ decomposition to CaO. An additional weight loss observed at 420-460 °C indicated the presence of $Ca(OH)_2$ species (Fig. 2B and C) by comparing with the corresponding authentic sample [27]. It is likely that the formation of $CaCO_3$ was retarded in the presence of Zn^{2+}. The relative concentration of OH^- and CO_3^{2-} is an important factor determining the precipitate composition [34]. The faster precipitation of Zn^{2+} by forming a basic carbonate should result in a drop of CO_3^{2-} concentration. The remaining Ca^{2+} may be precipitated in the form of $Ca(OH)_2$. The shift of decomposition peak of Zn precipitate towards higher temperatures with increasing the amount of Zn implied that a larger amount of Zn^{2+} interacted strongly with anion, typically CO_3^{2-}.

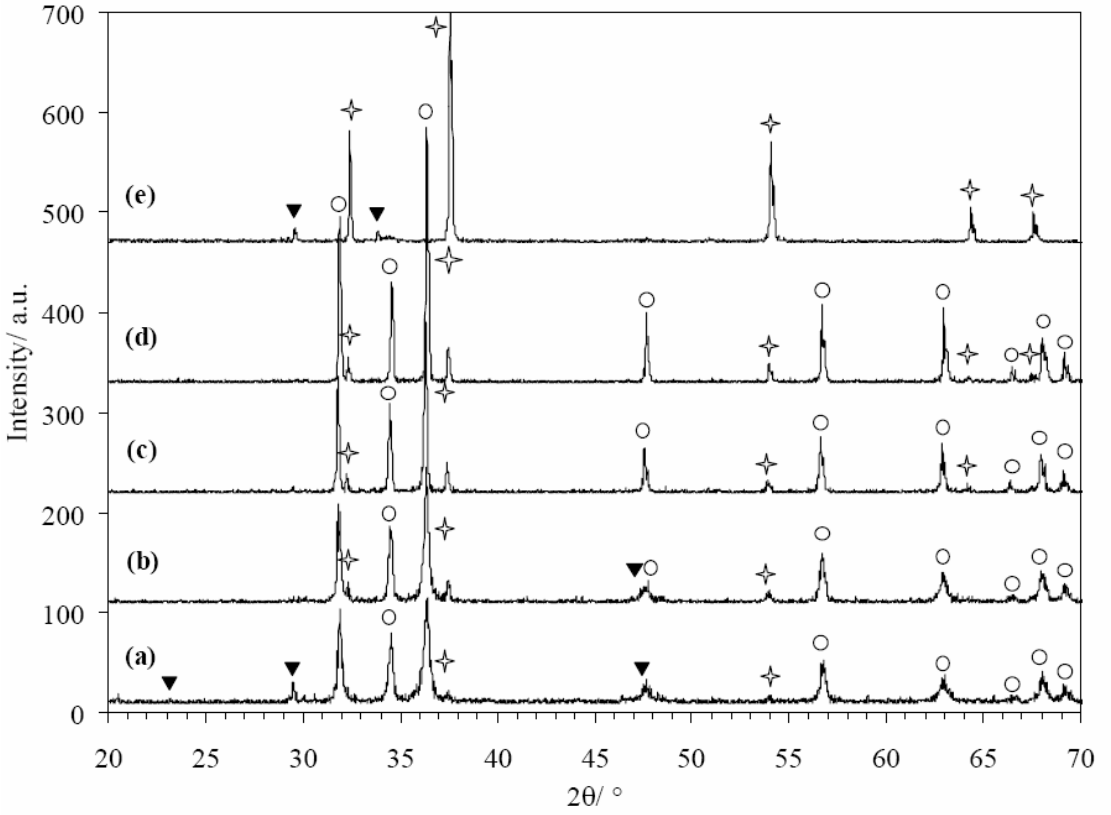


Fig. 3 XRD patterns of CaZn precipitates with the Ca/Zn atomic ratio of 0.25 after the calcination at 600 (a), 700 (b), 800 (c), and 900 (d). The pattern of pure Ca precipitate after the calcination at 800 °C is compared (e). (Symbols: ✧ = CaO, ▼ = $CaCO_3$ and ○ = ZnO)

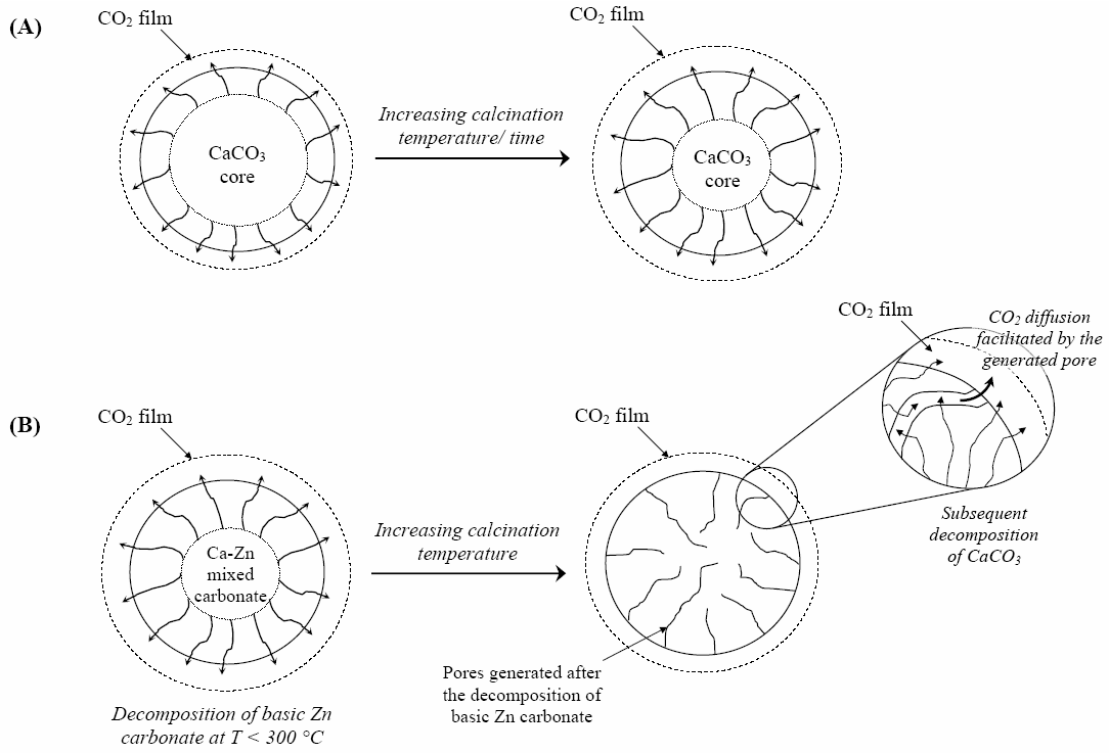
Figure 3 compares XRD patterns of CaZn precipitate with the Ca/Zn ratio of 0.25 after the calcination at 600-900 °C. The several diffraction peaks corresponding to $CaCO_3$ phase remained concomitantly with the presence of few weak peaks related to CaO when the calcination was performed at 600 °C (Fig. 3a). Similarly to the information from the TGA results (Fig. 2), basic Zn carbonate was completely

decomposed to ZnO at this temperature. At 700 °C, the amount of $CaCO_3$ was greatly reduced with an increase in the CaO peaks (Fig. 3b). No peaks of $CaCO_3$ were found when the calcination temperature rose to 800 °C (Fig. 3c). However, pure Ca precipitate showed a retention of the carbonate peaks up to this temperature (Fig. 3e). In addition, morphological studies on pure Ca and on CaZn mixed precipitate with the Ca/Zn ratio of 0.25 using SEM technique indicated that totally change of pure Ca precipitate with rhombohedron phase to CaO particles with rough surface (Fig. 1A) required the temperature as high as 800 °C while very small spherical particles, similarly to those of pure ZnO (Fig. 1F), were already present in the cases of mixed precipitate calcined at 600 °C.

It can be deduced from the results above that the formation of CaZn mixed precipitate significantly reduced the decomposition temperature of $CaCO_3$ to form CaO. The induced thermal decomposition of $MgCO_3$ by doping a small amount of Zn or Al was reported by El-Shobaky and Mostafa [35]. Since CaO is known to have much higher basicity than ZnO, CaO is considered as the main basic sites responsible for the transesterification. The lower the calcination temperature that is required for the decomposition of $CaCO_3$, the lower the energy that is consumed in the preparation of active catalyst. In addition, the peaks related to CaO and ZnO phases became more intense with increasing the calcination temperature to 900 °C. The size estimation of CaO and ZnO nano-clusters in the mixed precipitate treated between 700 and 900 °C revealed an increase in the size from 37.3 and 26.6 nm to 46.6 and 41.3 nm, respectively, with elevating the calcination temperature, reflecting the cluster agglomeration, possibly via a sintering.

The combination of particle size reduction and previous loss of H_2O and CO_2 from basic Zn carbonate should provide an explanation for the ease of $CaCO_3$ decomposition upon the addition of Zn. Models for the thermal decomposition of $CaCO_3$ and CaZn precipitate were proposed in Scheme 1. Generally, the decarbonation is a reversible reaction that strongly depends on CO_2 concentration in the atmosphere and on the elemental composition and particle size of carbonate compound [19]. The CO_2 dissociation always proceeds from the outside surface inward (Scheme 1A). The previous CO_2 evolved may form a film covering the particle surface during the progressive dissociation of interior particles, enhancing the possibility of CaO recarbonation to $CaCO_3$. In the presence of Zn hydroxide and/or carbonate, a number of voids are generated via the decomposition to ZnO (Scheme 1B). These voids should facilitate the heat transfer into interior particles and the diffusion of the gaseous product.

Moreover, since the particle size is reduced by forming CaZn mixed precipitate, the distance for CO_2 diffusing out of the particle is decreased, reducing the temperature required for the decomposition of $CaCO_3$.



Scheme 1 Proposed models for decomposition of pure Ca precipitate (A) and mixed precipitate of Ca and Zn (B).

4.2 Transesterification over CaZn Catalysts

Table 2 compares the activity of CaZn catalysts prepared by using different methods in the transesterification of palm kernel oil (PKO). CaO synthesized via co-precipitation with Na_2CO_3 exhibited comparable activity to that of CaO derived from natural calcite (46.2 %). $CaCO_3$ itself was not active. The TGA analysis indicated that calcite and pure Ca precipitate had a similar decomposition temperature and weight loss (not shown here). Due to its low basicity, the calcined Zn precipitate gave a negligible amount of methyl esters. The mixed oxides of Ca and Zn prepared via co-precipitation enhanced the methyl ester formation. However, using Na_2CO_3 as the precipitant resulted in more active CaZn catalyst. The ME content of 93.5 % can be achieved. This result should be attributed to an incomplete precipitation between metal ions and CO_3^{2-}, related to the ease of $(NH_4)_2CO_3$ decomposition in hot water [36]. CaZn-1 synthesized via the urea hydrolysis gave the ME content of 27.6 %. The mixed precipitate attained was suggested to form a mixed hydroxide [28]. In the presence of different bases, the

relative concentration of OH^-/CO_3^{2-} in the synthesis mixture should increase in the order: Na_2CO_3 solution < $(NH_4)_2CO_3$ solution < urea solution. The results emphasized that CaZn derived from the corresponding mixed metal carbonate precursor has higher transesterification activity than that prepared through thermal dehydroxylation of the related mixed metal hydroxide [27].

Table 2 Comparison of methyl ester content[a] obtained over CaZn catalysts synthesized via different methods

Catalyst[b]	Synthesis method	Methyl ester content (wt.%)
CaO	Co-precipitation with Na_2CO_3	46.2
CaO	Natural calcite	46.8
$CaCO_3$[c]	Natural calcite	1.7
ZnO	Co-precipitation with Na_2CO_3	0.4
CaZn-1	Co-precipitation with Na_2CO_3	93.5
CaZn-1	Co-precipitation with $(NH_4)_2CO_3$	73.9
CaZn-1	Urea hydrolysis	27.6

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

[b] Calcined at 800 °C for 2 h prior to use in the reaction.

[c] Non-calcined calcite.

The effect of Ca/Zn atomic ratio on the PKO transesterification activity of CaZn catalysts is shown in Fig. 4. It can be seen that the ME content was greatly dependent on the Ca/Zn ratio. The catalysts with low Zn content, the Ca/Zn ratios of 4 and 1.5, exhibited low methyl ester formation. When the amount of Zn was increased to the Ca/Zn ratio of 1, the ME content was enhanced remarkably to 93.5 %. However, further introduction of Zn into the catalyst to the ratio of 0.67 and 0.25 did not alter the ME content much. The enhancement of transesterification activity by forming CaZn mixed oxide should be due to a combination of the increase in the surface area (Table 1) and the complete decomposition of mixed carbonate precursors, generating active CaO sites (Fig. 2 and 3). Given the present results, CaZn with the Ca/Zn ratios of 0.25-1 were the most suitable catalyst for the transesterification of PKO.

As discussed for the XRD results (Fig. 3), the presence of CaO is strongly dependent on the calcination temperature. The results of PKO transesterification shown

in Fig. 5 suggest that the temperature of 600 °C was too low to effectively decompose $CaCO_3$ and to generate a sufficient amount of active CaO. Although a small amount of $CaCO_3$ still remained after the calcination at 700 °C (Fig. 3b), the ME content as high as 93.0 % can be attained. 800 °C is the suitable calcination temperature, resulting in the complete decomposition of carbonate species (Fig. 3c) and the most active CaZn-0.25 catalyst, giving the ME content of 94.2 %. The calcination at higher temperature (900 °C) significantly decreased the ME content. This result should be due to the sintering effect causing an agglomeration of CaO and ZnO clusters (Fig. 3). Boynton reported a hard burn effect relating to the calcination of limestones at high temperatures, resulting in a dense and unreactive lime [19].

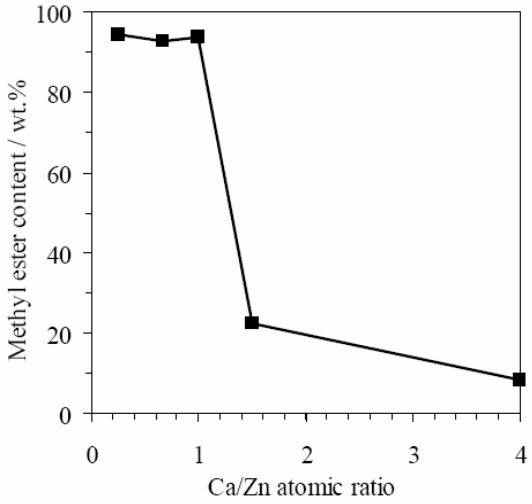


Fig. 4 Dependence of methyl ester content on the Ca/Zn atomic ratio of CaZn catalyst. Reaction conditions: methanol/oil molar ratio, 30; catalyst amount, 10 wt.%; time, 3 h; temperature, 60 °C.

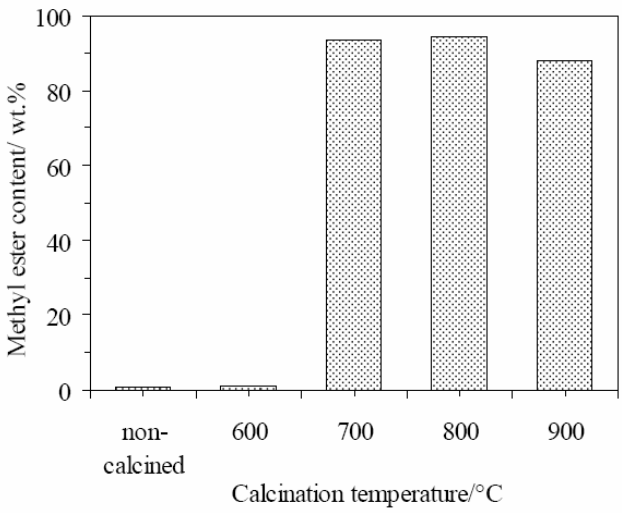


Fig. 5 Dependence of methyl ester content on calcination temperature of CaZn-0.25 catalyst. Reaction conditions: methanol/oil molar ratio, 30; catalyst amount, 10 wt.%; time, 3 h; temperature, 60 °C.

Figure 6 reveals the effect of catalyst amount on the methyl ester formation in the transesterification of PKO over CaZn-0.25. In the absence of catalyst, there were no methyl esters formed in the reaction. Applying the catalyst amount of 10 wt.% yielded the highest ME content of 94.2 % within 3 h. Reducing the catalyst amount to 2-6 wt.% slightly decreased the ME content to ca. 92.5 %. When the catalyst amount was further decreased to less than 2 wt.%, the formation of methyl esters decreased remarkably to less than 20 %. This result implies that the transesterification of PKO is strongly dependent on the amount of basic sites. It was suggested from comparative studies of various solid base catalysts in the transesterification of soybean oil and the isomerization of 1-butene 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 [12]. From this study, we can conclude that the suitable amount of CaZn-0.25 required for the transesterification of PKO is in the range of 2-10 wt.%.

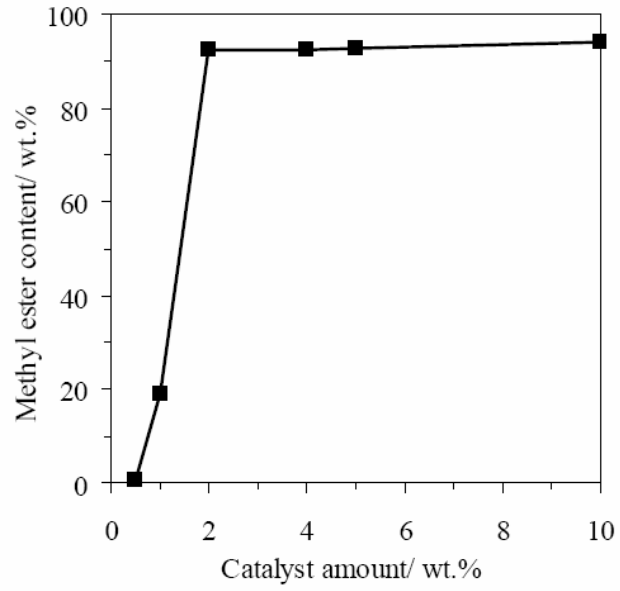


Fig. 6 Dependence of methyl ester content on amount of CaZn-0.25 catalyst. Reaction conditions: methanol/oil molar ratio, 30; time, 3 h; temperature, 60 °C.

The effect of methanol/oil molar ratio on the formation of methyl esters over CaZn-0.25 is illustrated in Fig. 7. It was found that, at the catalyst amount of 10 wt.%, the ME content was slightly increased from 91.6 to 94.2 % when the methanol/oil molar ratio increased from 10 to 30. Upon further addition of methanol to reach the ratio of 50, it can be seen that the ME content was not significantly altered. When the amount of catalyst was decreased to 3 wt.%, the highest ME content was also achieved at the methanol/oil ratio of 30. Thus, the appropriate molar ratio of methanol/oil for the transesterification of PKO over CaZn-0.25 is 30.

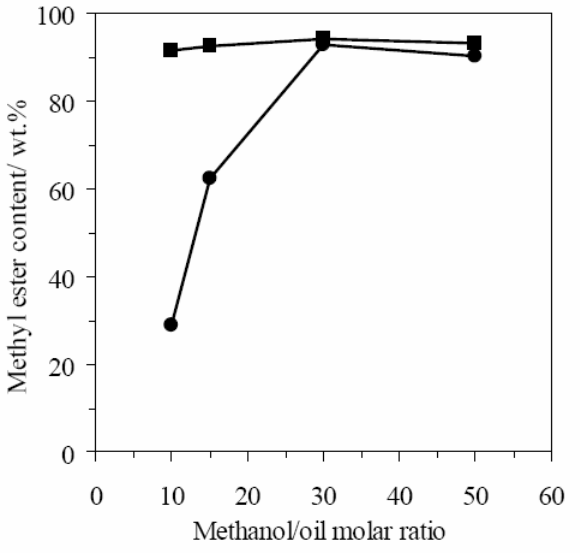


Fig. 7 Dependence of methyl ester content on methanol/oil molar ratio over CaZn-0.25 catalyst. Reaction conditions: catalyst amount, 3 (●) and 10 (■) wt.%; time, 3 h; temperature, 60 °C.

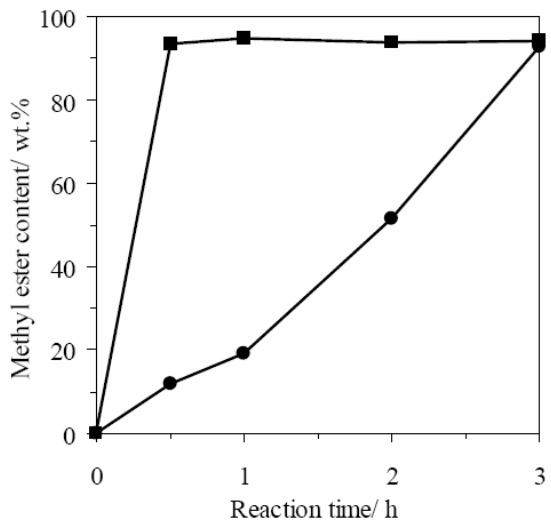


Fig. 8 Dependence of methyl ester content on reaction time over CaZn-0.25 catalyst. Reaction conditions: methanol/oil molar ratio, 30; catalyst amount, 3 (●) and 10 (■) wt.%; temperature, 60 °C.

Figure 8 shows the dependence of the ME content on the reaction time over CaZn-0.25. The results indicate that the CaZn catalyst is very active, giving the ME content as high as 93.4 % within 30 min when using the amount of catalyst of 10 wt.%. The ME content was slightly improved to 94.8 % after prolonging the reaction time to 1 h. However, there was no significant change in the ME content when the reaction time was extended longer. At the catalyst amount of 3 wt.%, the reaction required 3 h to attain a similar ME content. Since our CaZn catalyst is relatively cheap and easy to synthesize, shortening the reaction time to 1 h by applying 10 wt.% catalyst is more favorable for industrial application. Moreover, tests of CaZn catalyst in the

transesterification of various vegetable oils indicated that the synthesized CaZn-0.25 can be also used in the biodiesel production from palm olein oil, soybean oil, and sunflower oil, giving the ME content of > 94 %.

4.3 Regeneration and Reusability of CaZn Catalysts

Reusability is one of the most important features of a heterogeneous catalyst for its commercialization. In this study, three types of regeneration procedures were applied. The regeneration via a hydrothermal treatment was performed by washing the used CaZn catalyst with methanol, followed by the calcination in a muffle furnace at 500-800 °C for 2 h. Other regeneration methods were carried out by thoroughly washing the spent catalyst with pure methanol or with a mixture of methanol and 5 M NH_4OH solution, followed by drying in an oven at 100 °C. The transesterification activity of regenerated CaZn catalysts is compared in Fig. 9. It can be seen that the methanol washing could not recover the activity of mixed oxide catalyst. The ME content was remarkably reduced to 54.9 % in the second successive use. The elemental analysis by

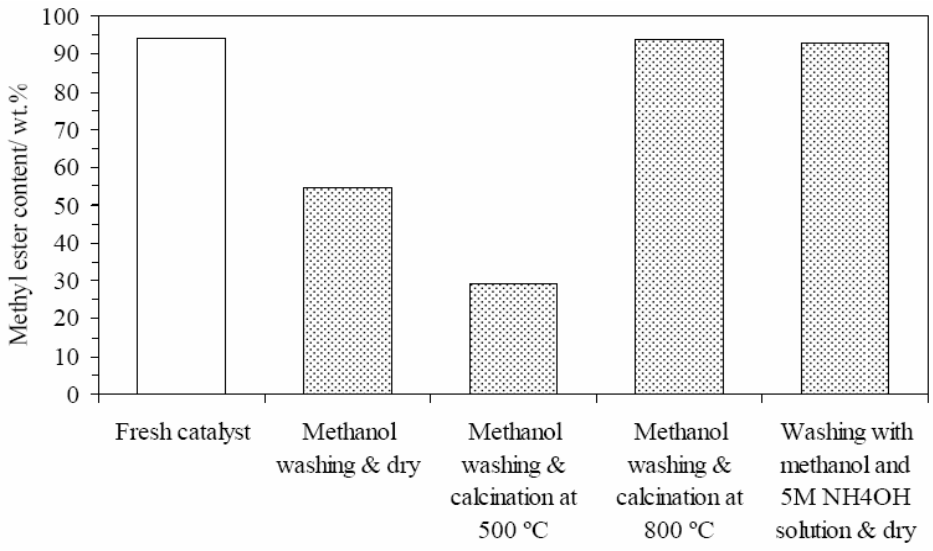


Fig. 9 Effect of regeneration methods on methyl ester formation over CaZn-0.25 catalyst. Reaction conditions: methanol/oil molar ratio, 30; catalyst amount, 10 wt.%; time, 1.5 h; temperature, 60 °C.

XRF technique revealed that the Ca/Zn ratio of spent CaZn catalyst washed with methanol (Ca/Zn = 0.22) was not different to that of fresh one (Ca/Zn = 0.23), indicating a small leaching of active CaO sites during the transesterification and the regeneration. These results suggested that the loss of transesterification activity in the present case is not mainly derived from the dissolution of active metal.

To further investigate the cause of catalyst deactivation, we compared the thermal analysis results of spent mixed oxide catalyst before and after methanol washing using TGA technique (Fig. 10). The comparison revealed that the spent CaZn catalyst before the washing contained organic deposits more than 12 wt.% (Fig. 10A), including methyl esters, glycerol, and mono-/di-glycerides, corresponding to the weight loss appearing at 204, 316, and 389 °C, respectively. The weight loss at 664 °C was derived from dehydroxylation/decarbonation of the catalyst itself, as suggested by an endothermic change of DTA curve (not shown here). After the regeneration by methanol washing, a significant amount of organic parts still remained (4.4 wt.%) (Fig. 10B – thick line), suggesting that the loss of transesterification activity of mixed oxide is due to the deposition of organic materials on the active surface.

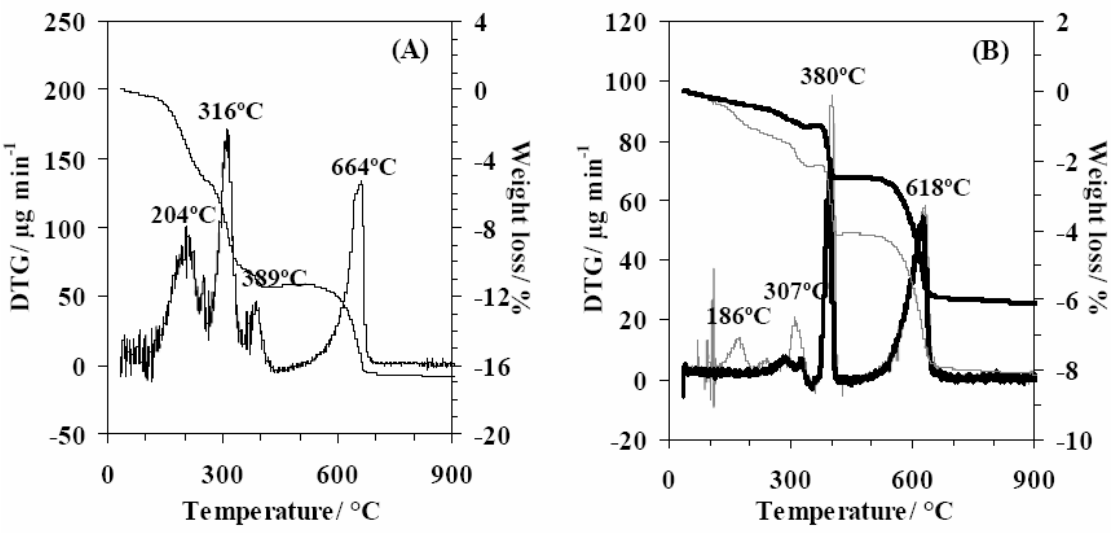


Fig. 10 Weight loss and DTG curves of spent CaZn-0.25 catalyst (A) and after regeneration by washing with methanol (B – thin line) or with a mixture of methanol and 5 M NH_4OH (B – thick line).

As shown in Fig. 9, by the subsequent thermal treatment at 800 °C, the catalytic activity of CaZn can be recovered. This indicates the removal of organic deposit by air oxidation. Lowering the calcination temperatures to 500 °C resulted in the formation of grayish catalysts, and a severe loss of the ME content. Alternatively, the spent catalyst after being washed with a mixture of methanol and 5 M NH_4OH solution exhibited a high ME content comparable to the fresh one. The TGA results (Fig. 10B – thin line) revealed that this regeneration method can remove the organic deposit more efficiently than the methanol washing. This success should be due to the fact that polar molecules like glycerol and mono-/di-glycerides are more soluble in water than in methanol. The CaZn catalyst can be repeatedly used up to 3 times with maintaining the ME content over 90 % by the treatment with the mixture of methanol and 5 M NH_4OH solution.

5. Conclusions

In the present study, we have synthesized CaZn mixed oxides, and investigated their catalytic performances in the transesterification of PKO. CaO and ZnO in the mixed oxide particles prepared by the co-precipitation method were present as nano-clusters. The sizes of both clusters were increased with the Ca/Zn atomic ratio. Increasing the amount of Zn (decreasing the Ca/Zn ratio) resulted in the morphological change and the reduction of particle size, concomitantly with the increase in the surface area. The combination of TGA, SEM, and XRD results indicated that the formation of CaZn mixed oxide decreased the calcination temperature required for the decomposition of $CaCO_3$.

The active mixed oxide of Ca and Zn for the transesterification can be successfully prepared by the co-precipitation of corresponding mixed metal nitrate solution in the presence of Na_2CO_3 as precipitant. The suitable Ca/Zn ratio and calcination temperature to prepare an active CaZn mixed oxide are in the range of 0.25-1 and 800 °C, respectively. By varying the transesterification conditions at 60 °C, one can achieve the ME content > 94 % when the reaction parameters were set as follows: the methanol/oil ratio = 30, the amount of CaZn catalyst with the Ca/Zn ratio of 0.25 = 10 wt.% (based on weight of the oil), and the reaction time = 3 h. Washing with the mixture of methanol and 5 M NH_4OH is a good method for the regeneration of a spent catalyst. Our prepared CaZn catalyst can be reused up to 3 times with maintaining the ME content > 90 %.

6. Suggestion for Future Research

1. To improve catalytic stability and durability of CaZn mixed oxide catalyst.
2. To test CaZn mixed oxide catalyst in a continuous process, for instant a fixed bed reactor, for biodiesel production.
3. To study on preparation, characterization and catalytic activity of 3-component mixed oxides for the transesterification of palm kernel oil with methanol.

Output จากโครงการวิจัยที่ได้รับทุนจาก สกว.

1. ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

C. Ngamcharussrivichai, P. Totarat, K. Bunyakiat “Ca and Zn mixed oxide as a heterogeneous base catalyst for transesterification of palm kernel oil” *Applied Catalysis A: General* (2008) Vol. 341 Page 77-85. (Impact Factor = 3.166)

2. การเสนอผลงานในที่ประชุมวิชาการนานาชาติ

Totharat, P.; Bunyakiat, K.; Ngamcharussrivichai, C. “Biodiesel Production through Transesterification of Palm Kernel Oil over Mixed Calcium Oxide Catalysts” *6th Asia Pacific Conference on Sustainable Energy and Environmental Technology*, Bangkok, Thailand, May 7 – 11, 2007.

3. การจดสิทธิบัตร

ชวลิต งามจรัสศรีวิชัย, ปรางค์สินันท์ โทธรัตน์, กัญจนา บุณยเกียรติ “การผลิตไบโอดีเซลจากน้ำมันพืชผ่านการเร่งปฏิกิริยาทรานส์เอสเทอริฟิเคชันด้วยโลหะออกไซด์ผสม” (ยื่นขอจดสิทธิบัตรวันที่ 9 กุมภาพันธ์ พ.ศ. 2550)