

# Modified dolomites as catalysts for palm kernel oil transesterification

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## Abstract

Heterogeneously catalyzed transesterification of palm kernel oil with methanol over various modified dolomites has been studied at 60 °C. The modification of dolomite was performed via a conventional precipitation method using various nitrate salt solutions of alkali earth metals and trivalent metals. Influences of a variety of metals, calcination temperature of the parent dolomite, methanol/oil molar ratios, reaction time, catalyst amount, and catalyst reuse have been investigated. The results indicated that the calcination temperature of the parent dolomite is a crucial factor affecting the activity and the basicity of the resulting catalyst. The catalyst modified from dolomite calcined at 600 and 700 °C, followed by the precipitation from  $\text{Ca}(\text{NO}_3)_2$  and the subsequent calcination at 800 °C, exhibited the most active catalyst, giving the methyl ester content as high as 99.9% under the suitable reaction conditions, the methanol/oil molar ratio of 15, amount of catalyst of 10 wt.%, and reaction time of 3 h. As suggested by the TGA results, the high activity of the catalyst should be due to the presence of two active CaO sites generated from the precipitated  $\text{Ca}(\text{OH})_2$  located in the crystalline phase of dolomite and from  $\text{CaCO}_3$  remaining after the calcination of the parent dolomite at 600–700 °C. © 2007 Elsevier B.V. All rights reserved.

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## 1. Introduction

Biodiesel is mono-alkyl esters of fatty acids derived from vegetable oils and animal fats. It has received much attention as an alternative green fuel due to its non-toxic, sulfur- and aromatic-free, biodegradable and renewable features [1]. Physical and fuel properties of biodiesel are categorized into the range of petroleum-based diesel fuel. Thus, it can be applied to compression-ignition diesel engines with little or no modifications. Additional advantage is that, like any other biomass-derived fuels, the exhaust gas from biodiesel combustion contains no  $\text{SO}_x$ , relatively small amount of CO, unburnt hydrocarbons and particulate matter, compared to that from the combustion of conventional diesel fuel [2–4].

Conventional biodiesel production is performed through a transesterification of triglycerides in vegetable oils and animal fats with mono-alkyl alcohols, for example methanol and ethanol, in the presence of homogeneous base [5–8] or acid [9–11] catalysts. However, these homogeneous catalysis sys-

tems have many drawbacks. Removal of these catalysts to purify the biodiesel fuel and glycerol as a by-product is difficult and requires a large amount of water. Consequently, a considerable amount of wastewater is inevitably produced. To overcome these problems, the transesterification over environmentally benign solid catalysts is a promising route.

A number of articles reporting on development of heterogeneous catalysts for transesterification of various oils with methanol have been published [12–16]. Natural calcium carbonate rock is a cheap catalyst but its activity was low and a high reaction temperature was required to achieve the conversion of >95% [12]. On the other hand, Kim et al. [13] used  $\text{Na}/\text{NaOH}/\gamma\text{-Al}_2\text{O}_3$  as a strong base catalyst to the transesterification of soybean oil, showing performance comparable to the conventional homogeneous  $\text{NaOH}$  catalyst.  $\text{Al}_2\text{O}_3$ -supported potassium oxides derived from carbonate [14], nitrate [15] and iodide [16] salts of potassium were also active. However, the catalysis over these supported alkali metal oxides has been considered to occur through the homogeneous route to a significant extent [17,18], since the oxides of alkali metal group are generally water-soluble [19]. Consequently, the major drawbacks of homogeneous catalysis could not be technically resolved by using these types of catalysts. In contrast, oxides of alkali earth

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metals are less soluble in water [19]. Even though this group of oxides is less basic compared to the former group, under suitable preparation and transesterification conditions they should exhibit a good catalytic performance [18].

Dolomite is a naturally abundant rock found in several areas of Thailand. At present, a major domestic usage of dolomite is cement manufacturing and landfill due to its very low cost. Dolomite mainly consists of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  with a small amount of ferrite and silica. Like calcite, pure  $\text{CaCO}_3$ , upon a simple calcination at high temperatures, the carbonate groups of dolomite are decomposed, and highly basic  $\text{CaO}$  and  $\text{MgO}$  are generated. To our best knowledge, dolomite has received, however, less attention in the basic catalyzed chemical syntheses, in spite of its high basicity, low cost, less toxicity, and environmental friendliness. Therefore, we have examined the activity of modified dolomite catalysts for the transesterification of vegetable oil. The modified dolomites were prepared via a conventional precipitation from various nitrate salt solutions of alkali earth metals and trivalent metals on the parent dolomites calcined at different temperatures. Influences of metal types, calcination temperatures for the parent dolomite, methanol/oil molar ratio, reaction time, catalyst amount, and catalyst reusability have been investigated. The results indicated that, under the suitable reaction conditions, the dolomite modified with  $\text{Ca}(\text{NO}_3)_2$  proved to be the most active catalyst, giving the methyl ester content as high as 99.9%. Moreover, the XRD and TGA results suggested the catalytically active sites responsible for the transesterification over these modified dolomites.

## 2. Experimental

### 2.1. Catalyst preparation

Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) used in the present study was brought from Surat Thani Province, Thailand. Elemental composition analysis with an ED-2000 energy dispersive X-ray fluorescence (XRF) spectrometer indicated that it is composed of  $\text{CaO}$  31.20%,  $\text{MgO}$  16.56%,  $\text{Fe}_2\text{O}_3$  298 ppm,  $\text{SrO}$  198 ppm and  $\text{CO}_2$  balance. Analytical grade nitrate salts of various metals including  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  from Ajax were used as received to prepare modified dolomites via a conventional precipitation method. The amount of metal loaded was fixed at 2 mmol metal per gram of dolomite. Typically, a dolomite calcined at temperature between 600 and 800 °C was dispersed in deionized water under vigorous stirring at 60 °C. An aqueous solution of a metal nitrate was then added dropwise into the slurry. The resulting mixture was further stirred vigorously for 4 h at the same temperature. The precipitated product was recovered by filtration, followed by washing with deionized water and drying overnight at 120 °C. Before being used as the catalyst, all of the parent and modified dolomites were calcined at 800 °C for 2 h. Hereafter, the catalysts are designated as Me/DM-X where Me, DM and X represent type of metal loaded, dolomite and calcination temperature of the parent dolomite, respectively.

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 caprylic 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                 |

### 2.2. Transesterification reaction

Refined palm kernel oil (PKO) was donated by Chumporn Palm Oil Industry Co., Ltd. The fatty acid composition and physicochemical properties of the oil are shown in Tables 1 and 2, respectively. Reaction was carried out in a 250-mL three-neck round bottom flask equipped with a condenser and a magnetic stirrer. Typically, 1 g calcined catalyst was suspended in a required volume of methanol (99.5%, commercial grade). Temperature of the mixture was kept at 60 °C by a water bath. Subsequently, the oil was added into the mixture under vigorous stirring. The methanol/oil molar ratio was varied between 15 and 50. After the course of reaction (1–3 h), the catalyst was separated by filtration and the reaction mixture was then loaded into a rotary evaporator to remove excess methanol. The methyl ester products were recovered in a separating funnel followed by washing with deionized water and drying with  $\text{Na}_2\text{SO}_4$ . Composition of the methyl ester products was analyzed with a Varian CP-3800 gas chromatograph (GC) equipped with an FID detector and a 30-m DB-1 capillary column. Percentage of methyl esters was calculated based on the standard method EN 14103 using methyl heptadecanoate as a reference standard.

### 2.3. Catalyst characterization

Crystallinity of the parent and modified dolomite catalysts was confirmed by powder X-ray diffraction (XRD) using a Rigaku DMAX 2200/Ultima + diffractometer equipped with  $\text{Cu K}\alpha$  radiation. Elemental analysis was performed on an ED-2000 energy dispersive X-ray fluorescence (XRF) spectrometer. BET

Table 2

Physicochemical properties of palm kernel oil used in the present study

| Properties  | Analysis results |
|---|------------------|
| Density at 15 °C (g/ml)                                 | 0.922            |
| Kinematic viscosity at 40 °C ( $\text{mm}^2/\text{s}$ ) | 28.52            |
| Free fatty acid (mg KOH/g oil)                          | 0.14             |
| Moisture content (%)                                    | 0.1              |
| Iodine value ( $\text{g I}_2/100 \text{ g oil}$ )       | 17.55            |

surface area was measured by N<sub>2</sub> adsorption–desorption technique on a Micromeritic ASAP 2020 surface area and porosity analyzer. Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer Pyris Diamond thermogravimeter (TG/DTA) at a ramping rate of 8 °C min<sup>-1</sup> under dry air flow.

### 3. Results and discussion

#### 3.1. Development of an active modified dolomite

Fig. 1 shows the methyl ester (ME) content in the biodiesel product attained via the transesterification of PKO over the parent and modified dolomite catalysts calcined at 800 °C. The dolomite used for the modification was calcined at 800 °C (DM-800) beforehand. It can be seen that the calcined parent dolomite itself was very active, giving a ME content as high as 96.1%. After the precipitation from metal nitrates, the catalysts resulted in the decreased ME content. In respect of the ME content, the activity of the catalysts was decreased in the following order: DM-800 > Ca/DM-800 > Ba/DM-800 > Al/DM-800 > Mg/DM-800 > La/DM-800. This result suggested that metals loaded by this procedure decrease basic sites and/or basic strength of the parent dolomite. According to N<sub>2</sub> adsorption–desorption measurement, the BET surface area of DM-800 before and after the precipitation from the metal nitrate salts was decreased in the order: DM-800 (36.4 m<sup>2</sup> g<sup>-1</sup>) > Ca/DM-800 (27.8 m<sup>2</sup> g<sup>-1</sup>) > Mg/DM-800 (26.0 m<sup>2</sup> g<sup>-1</sup>) > Al/DM-800 (24.1 m<sup>2</sup> g<sup>-1</sup>) > Ba/DM-800 (20.2 m<sup>2</sup> g<sup>-1</sup>) > La/DM-800 (19.4 m<sup>2</sup> g<sup>-1</sup>). Possibly, the precipitated metal hydroxides covering the surface of DM-800, the amount of catalytically active sites on the calcined parent dolomite was decreased. The results also implied that the active sites produced by the calcination of parent dolomite at 800 °C have higher basicity than those generated from the precipitated metal hydroxides. Nevertheless, among the catalysts prepared, the dolomites modified with Ca(NO<sub>3</sub>)<sub>2</sub> (Ca/DM-800) and Ba(NO<sub>3</sub>)<sub>2</sub> (Ba/DM-800) showed high ME contents, 95.0% and 89.2%, respectively. Being the most active and environ-

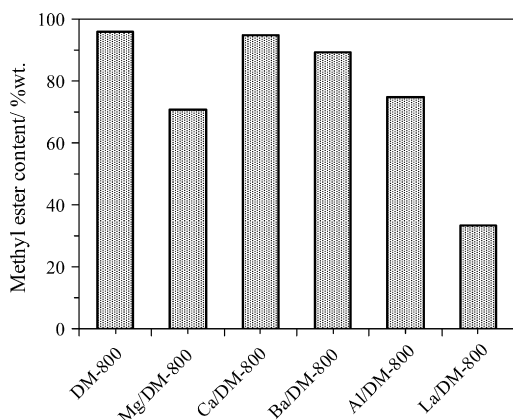


Fig. 1. Methyl ester content attained over dolomite and various modified dolomite catalysts after calcined at 800 °C. The parent dolomite used for the modification was calcined at 800 °C (DM-800). Reaction conditions: methanol/oil molar ratio, 50; catalyst amount, 10 wt.%; time, 3 h; temperature, 60 °C.

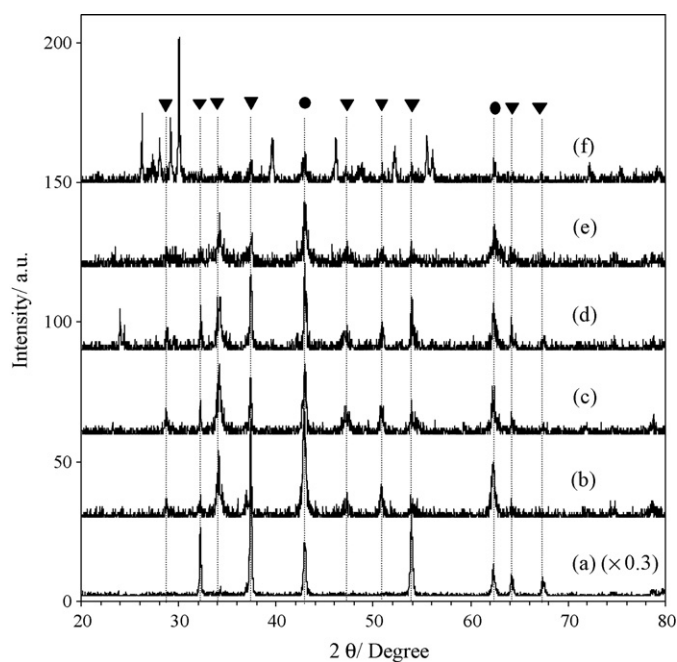


Fig. 2. XRD patterns of parent dolomite and various modified dolomite catalysts after calcined at 800 °C. The parent dolomite used for the modification was calcined at 800 °C. DM-800 (a), Mg/DM-800 (b), Ca/DM-800 (c), Ba/DM-800 (d), Al/DM-800 (e), and La/DM-800 (f), symbols: (▼) CaO and (●) MgO.

mentally friendly, Ca has been considered as the suitable metal for the preparation of modified dolomite as a catalyst for the transesterification.

It is generally accepted that the basicity of alkali earth metal oxides is higher than that of Al or La oxides. Zhang et al. found that the strength of basic sites of the alkali earth metal oxides studied with temperature-programmed desorption (TPD) of CO<sub>2</sub> increased in the order: MgO < CaO < SrO < BaO [20]. These suggest that the transesterification activity observed for the modified dolomites is not directly attributed to the basic strength of precipitated metal oxides. Fig. 2 illustrates the XRD patterns of DM-800 and the modified dolomite catalysts. DM-800 showed many reflection peaks at  $2\theta = 28.7^\circ, 32.3^\circ, 34.2^\circ, 37.3^\circ, 47.1^\circ, 50.9^\circ, 53.9^\circ, 64.2^\circ$  and  $67.4^\circ$ , indicating the predominance of CaO, while the peaks at  $2\theta = 43.1^\circ$  and  $62.4^\circ$  correspond to MgO. The XRD patterns of the modified dolomites also exhibited similar diffraction peaks but with much lower intensity, suggesting smaller amount of basic Ca and Mg oxides present in the calcined parent dolomite. The other small peaks observed for the modified dolomites indicated the presence of metal oxides derived from the corresponding nitrate salts used in the modification. It was seen that, among the modified dolomites, the total amount of CaO present, estimated from all of the related XRD peaks, was decreased in the following order: Ca/DM-800 > Ba/DM-800 > Al/DM-800  $\approx$  Mg/DM-800 > La/DM-800, which is in a similar order to the ME content attained (Fig. 1). On the other hand, the amount of MgO did not correlate with the catalytic activity. It is likely that the basic sites of the modified dolomites are mainly the CaO species present in the calcined parent dolomite, whereas the metal oxides generated from the precipitated metal hydroxides contribute a minor activity to the

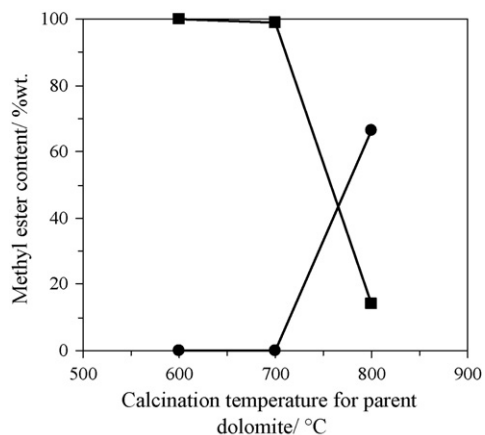


Fig. 3. Dependence of methyl ester content on calcination temperature of (■) parent dolomite used in the preparation of Ca/DM catalysts. For comparison, the effect of calcination temperature over (●) pure dolomite was shown. Before being applied to the transesterification, the Ca/DM catalysts were calcined at 800 °C. Reaction conditions: methanol/oil molar ratio, 15; catalyst amount, 10 wt.%; time, 3 h; temperature, 60 °C.

transesterification. Therefore, the key to the improvement of the catalytic activity of modified dolomites is to maintain the amount of accessible CaO sites in the parent dolomite during the modification step. Hereafter, we have focused on the development of a highly active dolomite modified with  $\text{Ca}(\text{NO}_3)_2$ .

To improve the activity of the Ca/DM catalyst, the calcination temperature of the parent dolomite before the modification was varied from 800 to 600 °C. For the reaction test, the methanol/oil molar ratio was decreased from 50 to 15. As shown in Fig. 3, it can be clearly seen that the calcination of parent dolomite at 700 or 600 °C before the modification increased the ME content to exceed 99%, while the catalyst prepared from the parent dolomite calcined at 800 °C (Ca/DM-800) exhibited the ME content of only 14.3%. This result suggested that the calcination of parent dolomite at 600–700 °C provides the Ca/DM catalysts with very high basicity and activity for the transesterification reaction. Hence, the suitable conditions for the preparation of highly active modified dolomite catalyst are the calcination of parent dolomite at 600–700 °C, followed by the precipitation from the  $\text{Ca}(\text{NO}_3)_2$  solution and the calcination of the resulting solid at 800 °C.

### 3.2. Effect of reaction conditions on the activity of Ca/DM-600 catalyst

Fig. 4 illustrates the effect of the methanol/oil molar ratios on the ME content over the Ca/DM-600 catalyst. There was no soap formation observed in all experiments. It can be seen that, at the ratio of 10, the ME content attained was 88.7%. Upon increasing the ratio to 15, a ME content as high as 99.9% was achieved. These results suggested that the amount of methanol at the ratios of 10 or lower is not sufficient to disperse oil and catalyst phases, and to facilitate the transesterification. It was reported that the heterogeneously catalyzed transesterification has a high mass-transfer limitation [15]. When the ratio was increased to 15, the mixture became more miscible, driving the

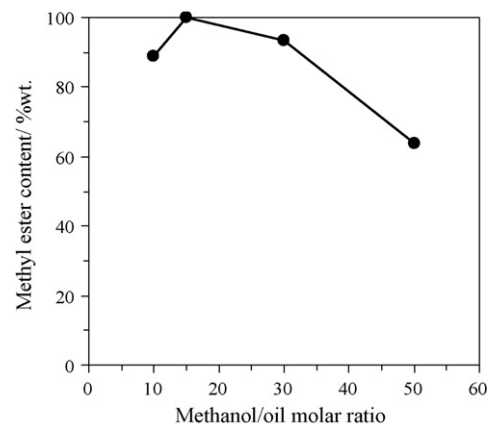


Fig. 4. Dependence of methyl ester content on methanol/oil molar ratio over Ca/DM-600 catalyst. Reaction conditions: catalyst amount, 10 wt.%; time, 3 h; temperature, 60 °C.

reaction towards more methyl ester formation. However, the ME content remarkably decreased when the ratio was increased to 30 and 50. It might be due to the reverse transesterification reaction [21].

In our experiment, we have found that, at the high ratios, the gravitational separation of methyl esters and glycerol was difficult; they formed a homogeneous phase. Normally, the methyl esters and methanol or glycerol are immiscible, so such a homogeneous phase is not expected in the absence of co-solvent, such as THF. Since the transesterification is a base-catalyzed reaction of a reversible nature, it is likely that the reverse transesterification occurs between the methyl ester product and glycerol, forming monoglycerides and diglycerides that behave molecularly like a co-solvent, and homogenize the products [22]. As a result, the ME content was decreased. Therefore, the optimum methanol/oil molar ratio in the present study is 15.

Effect of reaction time on the transesterification over the Ca/DM-600 catalyst was also studied. As shown in Fig. 5, at the first hour of the reaction, almost no methyl esters were formed. The ME content was increased when the reaction time was extended to 2 h (27.2%). At 3 h, the catalyst nearly com-

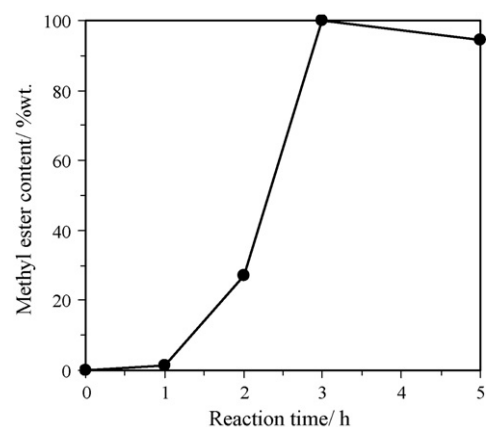


Fig. 5. Dependence of methyl ester content on reaction time over Ca/DM-600 catalyst. Reaction conditions: methanol/oil molar ratio, 15; catalyst amount, 10 wt.%; temperature, 60 °C.

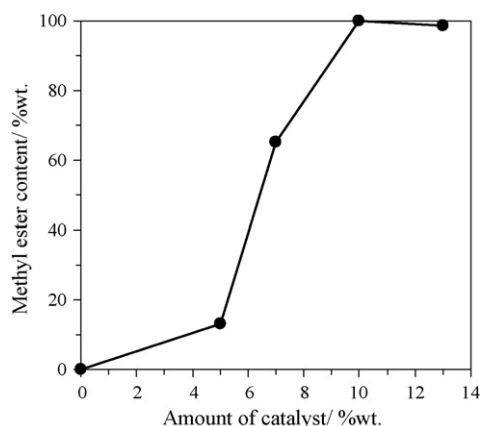


Fig. 6. Dependence of methyl ester content on amount of Ca/DM-600 catalyst. Reaction conditions: methanol/oil molar ratio, 15; time, 3 h; temperature, 60 °C.

pleted the transesterification, giving the ME content of 99.9%. As described earlier, the monoglycerides and diglycerides can facilitate the diffusion of reactants and products, and the transesterification in a similar way to co-solvents [22]. Therefore, the absence of methyl esters formed at the first hour and the rapid increase in the ME content after 2 h suggested the time required for the formation of sufficient amount of these triglyceride derivatives. On the other hand, it was found that the ME content was slightly decreased after prolongation of the reaction to 5 h. This may be also due to the reverse transesterification. These results indicated that the suitable reaction time required for obtaining the highest amount of methyl esters is 3 h.

Fig. 6 shows influence of amount of Ca/DM-600. The catalyst amount was varied between 5% and 12% by weight based on the amount of PKO used. It can be seen that the ME content increased from 13.0% to 99.9% with increasing amount of catalyst to 10 wt.%. This result suggests that the increased amount of methyl esters produced is due to an increase in the number of basic sites in the reaction system. Ebiura et al. reported that the activity of catalyst in the transesterification was closely related to the amount of basic sites, but not directly related to the basic strength [14]. Furthermore, increasing the catalyst amount to 12 wt.% did not much alter the ME content. From the study of effects of reaction conditions, it was concluded that the suitable conditions for the transesterification of PKO with methanol over the Ca/DM-600 catalyst, prepared from the parent dolomite calcined at 600 °C, followed by the precipitation from  $\text{Ca}(\text{NO}_3)_2$  and the calcination at 800 °C, are the methanol/oil molar ratio of 15, the amount of catalyst of 10 wt.%, and the reaction time of 3 h at the temperature of 60 °C.

Fig. 7 shows reusability of Ca/DM-600 catalyst in the transesterification of PKO. After the reaction and recovery by filtration, the catalyst was thoroughly washed with hexane, followed by air dry overnight. Before being used in each repetition, the catalyst was calcined at 450 °C for 2 h. It was revealed that Ca/DM-600 can be repeatedly used three times with the ME content over 95% maintained. Elemental analysis of the catalyst before and after being used in the reaction by the XRF technique indicated that, after the first use, there was only 1.5 wt.% CaO loss (Table 3). As a result, the transesterification activity of the cata-

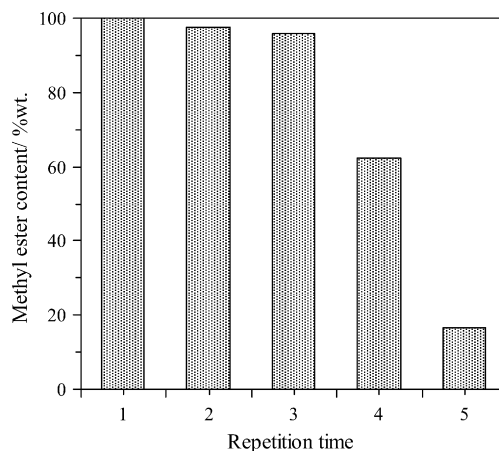


Fig. 7. Reusability of Ca/DM-600 catalyst in the transesterification of palm kernel oil. Reaction conditions: see Fig. 3.

lyst was retained. However, in the fourth and fifth runs, the ME content remarkably decreased to 62.2% and 16.5%, respectively (Fig. 7). The elemental composition of the catalyst after the fifth run suggested that the decline in the activity is related to the loss of active CaO species, as revealed by the amount of CaO that decreased by 9.3 wt.% (Table 3). Although our Ca/DM-600 catalyst is reusable only a few times, the dolomite is very cheap and available in many parts of Thailand, and the present modification is easy to perform. Therefore, we believe that the modified dolomites have a potential for being further developed for a large-scale production of biodiesel under heterogeneous catalysis conditions.

### 3.3. Clarification of the activity of modified dolomite catalysts

To clarify the catalytically active sites of modified dolomites, additional experiments on the reaction test and characterization by means of TGA were carried out over the parent and modified dolomites. According to Fig. 3, under the same reaction conditions for the modified dolomites, DM-800 showed the ME content of 66.5%, whereas DM-700 and DM-600 yielded very low ME contents. It was reported that the calcination of dolomite at 600–700 °C is sufficient to decompose the carbonate in  $\text{MgCO}_3$ , giving MgO, but does not favorably decompose the carbonate in  $\text{CaCO}_3$  [23]. The generation of CaO by the thermal

Table 3  
XRF elemental composition analysis of parent dolomite and Ca/DM-600 before and after the reaction

| Component                      | Concentration in catalyst (wt.%) |                        |               |               |
|--------------------------------|----------------------------------|------------------------|---------------|---------------|
|                                | Dolomite <sup>a</sup>            | Ca/DM-600 <sup>b</sup> |               |               |
|                                |                                  | Fresh                  | After 1st run | After 5th run |
| MgO                            | 34.6                             | 28.9                   | 30.0          | 35.6          |
| CaO                            | 65.3                             | 71.0                   | 70.0          | 64.4          |
| Fe <sub>2</sub> O <sub>3</sub> | 623 ppm                          | 361 ppm                | 178 ppm       | –             |
| SrO                            | 414 ppm                          | 124 ppm                | –             | –             |

<sup>a</sup> CO<sub>2</sub> balance.

<sup>b</sup> The catalyst was calcined at 800 °C for 2 h prior to the analysis.

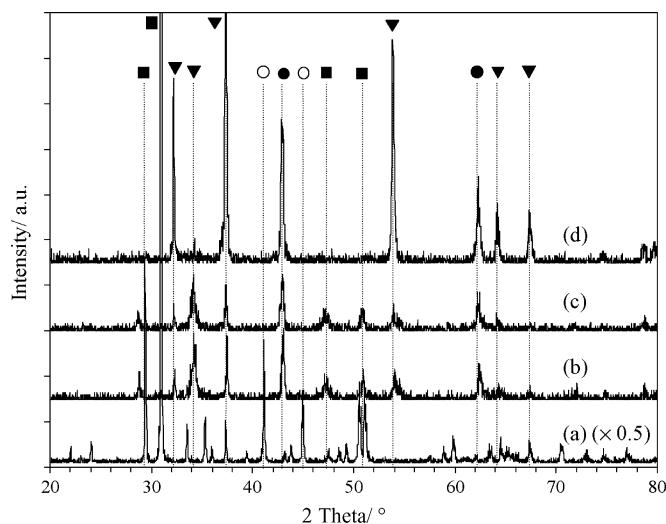


Fig. 8. XRD patterns of non-calcined dolomite (a) and dolomites calcined at 600 °C (b), 700 °C (c), and 800 °C (d), symbols: (▼) CaO; (●) MgO; (■) CaCO<sub>3</sub>; (○) MgCO<sub>3</sub>.

decomposition of CaCO<sub>3</sub> in dolomite occurs at temperatures in the range of 750–800 °C [23]. This suggested that CaO is more basic and has a more important role in the transesterification than MgO.

The XRD patterns of the non-calcined parent dolomite, DM-600, DM-700 and DM-800 are shown in Fig. 8. It can be seen that MgCO<sub>3</sub> and CaCO<sub>3</sub> in the non-calcined parent dolomite were decomposed to give MgO and CaO phases, respectively, to the various extents depending on the calcination temperature. At 600 and 700 °C, the diffraction peaks corresponding to the metal oxide phases were much less intense than those at 800 °C. Over DM-800, most of the metal carbonates related peaks disappeared concomitantly with the appearance of oxides as the dominant phase. Therefore, the calcination of dolomite at 800 °C is sufficient to generate a large amount of the basic metal oxides, and the resulting DM-800 is more active in the transesterification than DM-600 or DM-700.

During the preparation of modified dolomites, the accessible MgO and CaO generated after the calcination of parent dolomite at 800 °C (DM-800) would be transformed to Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub>, respectively, upon being dispersed in water as follows:

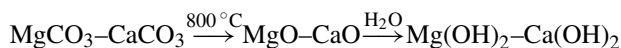


Fig. 9 compares weight loss, DTG (Fig. 9A) and DTA (Fig. 9B) curves of the parent dolomite before the calcination (DM) and the hydrated DM-800. The parent dolomite showed a major weight loss starting from 570 to 800 °C with a maximum of the DTG peak at 754 °C (Fig. 9A), corresponding to 47.5% loss of CO<sub>2</sub> (theoretical value = 52.2%) and 52.5% remaining in the form of MgO and CaO. The hydrated DM-800 also exhibited a similar decomposition pattern but with a more intense DTG peak. Furthermore, the DTA curve of the hydrated DM-800 presented a broad peak between 300 and 620 °C (Fig. 9B), suggesting the formation of Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub> (by comparing with that of the authentic samples).

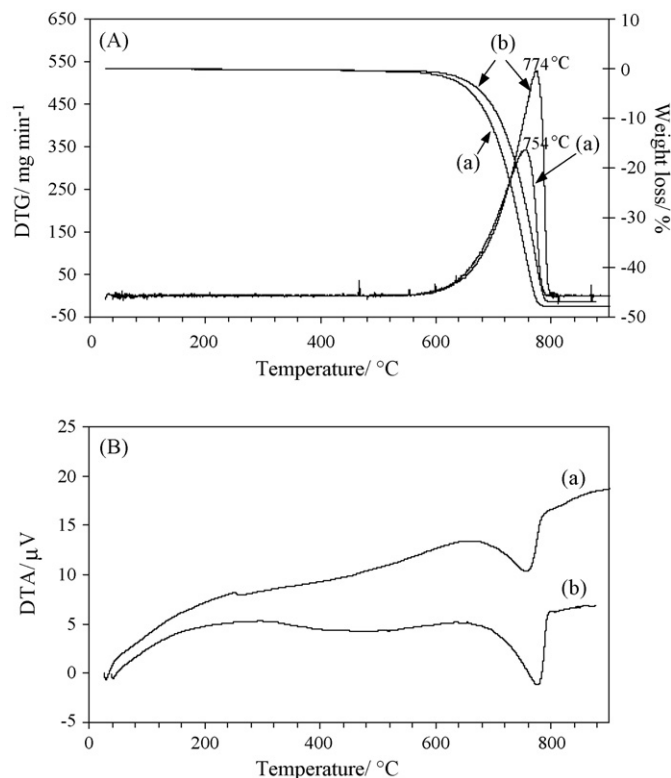


Fig. 9. Thermogravimetric analysis (TGA) of non-calcined dolomite (DM) (a) and hydrated DM-800 (b). Weight loss and DTG curves are shown in (A), and DTA curves are shown in (B).

However, there was no decomposition observed in this temperature range from the weight loss and DTG curves, indicating a small amount of these hydroxide species. Perhaps, these species were formed from Mg and Ca ions leached from DM-800 upon the hydration, and present as a phase separate from the dolomite particles. It is interesting to note that the high temperature DTG peak of the hydrated DM-800 was shifted to 774 °C, ca. 20 °C higher than that of DM (754 °C). This result suggested the formation of other types of Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub>, probably as accessible hydroxide species in a crystalline phase of the dolomite.

Fig. 10 reveals weight loss and DTG curves of the hydrated DM-800 and all Ca/DM catalysts. In contrast to that of the hydrated DM-800 (Fig. 10A), the decomposition pattern of Ca/DM-800 catalyst (Fig. 10D) exhibited a three-step weight loss. By comparing with the authentic samples, the DTG peak at 368 °C is attributed to the separate Mg(OH)<sub>2</sub>, while the DTG peak at 441 °C corresponds the loss of water from the separate Ca(OH)<sub>2</sub>. These more intense DTG peaks indicated that the amounts of the separate Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub> in Ca/DM-800, contributing the water loss of 8.7 and 3.6 wt.%, respectively, are higher than those in the hydrated DM-800 (Fig. 10A). It should be ascribed to more MgO and CaO leached from DM-800 after mixing with the Ca(NO<sub>3</sub>)<sub>2</sub> acid solution (pH ≈ 2) in the modification step. Moreover, the separate Ca(OH)<sub>2</sub> can be formed via a fast precipitation of Ca ions from the nitrate salt solution due to the highly basic mixture of DM-800 in water (pH ≈ 12). It is worth noting that the amount of water lost from the separate

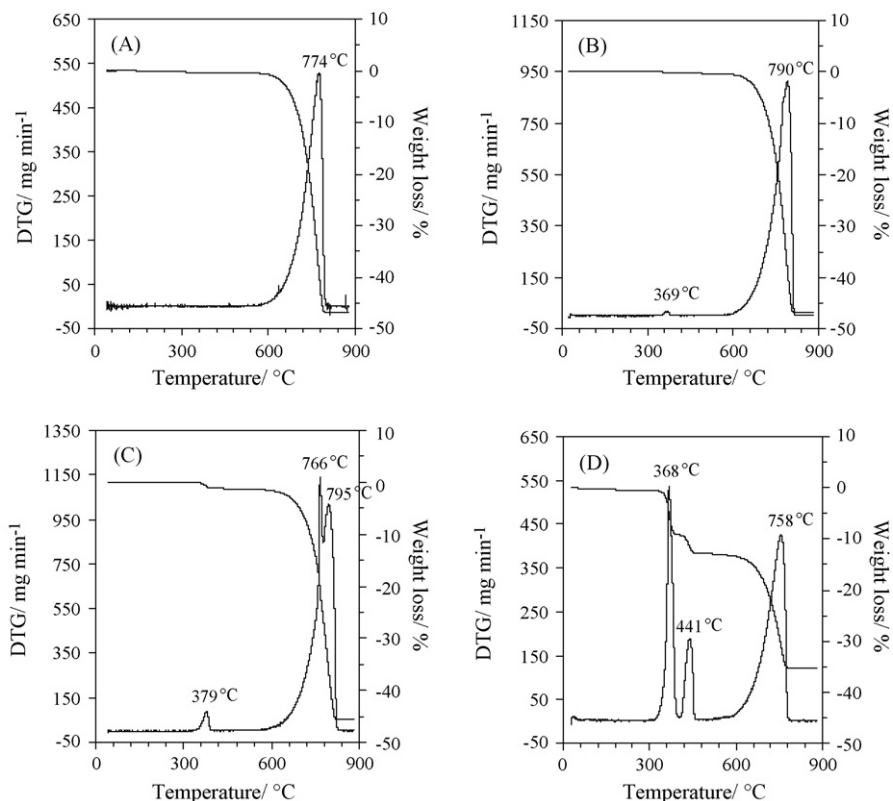
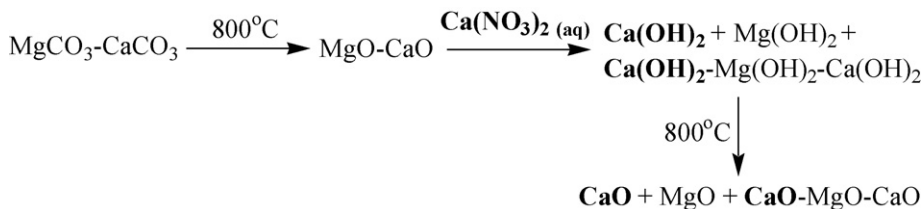


Fig. 10. Weight loss and DTG curves of hydrated Ca/DM-800 (A), Ca/DM-600 (B), Ca/DM-700 (C), and Ca/DM-800 (D).

$\text{Ca}(\text{OH})_2$  (3.6 wt.%) corresponds to  $2.0 \text{ mmol Ca g}_{\text{dolomite}}^{-1}$ , equal to the mole of  $\text{Ca}(\text{NO}_3)_2$  used in the modification.

Like the hydrated DM-800 (Fig. 10A), the high temperature decomposition peak at  $760^\circ\text{C}$  indicated the presence of  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  in the crystalline phase. However, the water weight loss in this step was low, only 22.4% (for the hydrated DM-800, the weight loss was 46.5%). Since the amounts of  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  in the crystalline phase of dolomite are directly correlated to the amounts of accessible MgO and CaO generated after the final calcination of Ca/DM-800 at  $800^\circ\text{C}$ , this result suggests that the amount of active metal oxides present in DM-800 is decreased by the modification. It should be related to a decrease in the number of accessible metal oxides on DM-800 by the Ca hydroxide precipitated on the surface of DM-800, as suggested by the decrease in the BET surface area described above. The phenomenon occurring during the preparation of Ca/DM-800 catalyst could be as follows:



The transesterification over carbonates and hydroxides of Mg and Ca calcined at  $800^\circ\text{C}$  indicated that MgO derived from either  $\text{MgCO}_3$  or  $\text{Mg}(\text{OH})_2$  is much less active than CaO from  $\text{CaCO}_3$  and  $\text{Ca}(\text{OH})_2$ . The former exhibited the ME content lower than 2%, while the latter gave the ME content of ca. 85%.

In consideration of the active sites in Ca/DM-800, MgO derived from either the separate  $\text{Mg}(\text{OH})_2$  or  $\text{Mg}(\text{OH})_2$  in the crystalline phase of dolomite can be neglected because of its very low activity. Thus, there were essentially two types of active sites responsible for the transesterification over the Ca/DM-800 catalyst: CaO derived from the separate  $\text{Ca}(\text{OH})_2$  and that generated by dehydroxylation of  $\text{Ca}(\text{OH})_2$  in the crystalline phase.

The TGA results obtained from DM-800 modified with the nitrate salts of Mg, Ba, Al, and La showed a similar decomposition pattern to Ca/DM-800 (Fig. 11). There were separate  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  as indicated by the DTG peaks at  $361\text{--}377^\circ\text{C}$  and  $431\text{--}530^\circ\text{C}$ , respectively. Moreover, the presence of Mg and Ca hydroxides in the crystalline phase was revealed by the DTG peaks at ca.  $733\text{--}757^\circ\text{C}$ . Compared to the total weight loss of the hydrated DM-800 (46.5%) in Fig. 10A, all modified dolomites exhibited much lower total amount of water lost (29.1–37.6%) in the same temperature range. It was

found that, like Ca/DM-800, the decrease in the total weight loss was mainly due to the decrease in the amount of water lost from the  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  in the crystalline phase of DM-800. It should be attributed to the reduced amount of accessible oxides on the surface of DM-800 after precipitated from the metal

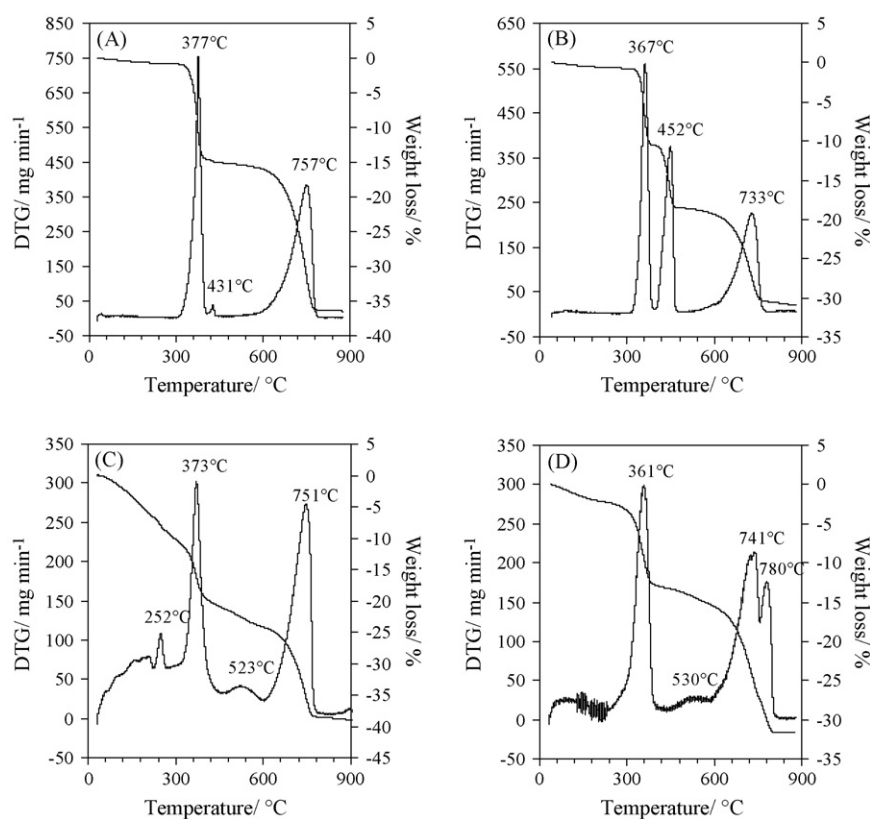


Fig. 11. Weight loss and DTG curves of Mg/DM-800 (A), Ba/DM-600 (B), Al/DM-700 (C), and La/DM-800 (D).

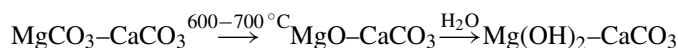
nitrate salts. The corresponding weight loss was declined in the order: Ca/DM-800 (22.4%) > Mg/DM-800 (21.3%) > Al/DM-800 (14.4%) > La/DM-800 (12.1%) > Ba/DM-800 (11.5%). This result also suggested that these modified dolomites have a small amount of active CaO sites derived from the crystalline part of DM-800 after the final calcination at 800 °C.

The formation of precipitated Mg(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>, Al(OH)<sub>3</sub>, and La(OH)<sub>3</sub> after the modification was also suggested by the decomposition patterns (Fig. 11) in comparison with the patterns of the authentic samples. The precipitated Mg(OH)<sub>2</sub> was decomposed at the same temperature as the separate Mg(OH)<sub>2</sub> (Fig. 11A), also implying its low activity in the transesterification, while the decomposition of Ba(OH)<sub>2</sub> occurred at nearly the same temperature as that of the separate Ca(OH)<sub>2</sub> (Fig. 11B). Dehydroxylation of Al(OH)<sub>3</sub> occurred at 252 °C (Fig. 11C) whereas the water lost from La(OH)<sub>3</sub> was found at 780 °C (Fig. 11D). Unfortunately, due to overlapping of several weight losses, the amount of each hydroxide species cannot be exactly calculated.

By estimating the mole of water lost from various hydroxides between 200 and 900 °C, excluding that from the separated Mg(OH)<sub>2</sub>, it was suggested that the total amount of basic oxides decreases in the following order: Ca/DM-800 (14.5 mmol g<sup>-1</sup>) > Al/DM-800 (13.0 mmol g<sup>-1</sup>) > Mg/DM-800 (12.1 mmol g<sup>-1</sup>) > La/DM-800 (10.3 mmol g<sup>-1</sup>) > Ba/DM-800 (7.7 mmol g<sup>-1</sup>). Except for Ba/DM-800, this order is close to the trend for the transesterification activity (Fig. 1), indicating that not only the active CaO sites in DM-800 but the oxides produced from the precipitate of metal nitrate salts also con-

tribute to the methyl ester formation, more or less depending on the basicity of the corresponding metal oxides. The deviation of Ba/DM-800 should be due to the presence of a weight loss at temperature >900 °C. It may be related to a highly basic Ba(OH)<sub>2</sub>. This hydroxide was not converted to BaO by the calcination of Ba/DM-800 at 800 °C before being used in the reaction. Although this catalyst possessed the smallest amount of the active CaO sites (see above), the contribution of Ba(OH)<sub>2</sub> may be relatively large due to its high basicity, resulting in a high ME content (Fig. 1).

Unlike that of Ca/DM-800 (Fig. 10D), the decomposition patterns of Ca/DM-600 (Fig. 10B) and Ca/DM-700 (Fig. 10C) exhibited a small weight loss of water from the separate Mg(OH)<sub>2</sub> at 370 °C without the decomposition step related to the separate Ca(OH)<sub>2</sub>. This result suggested a small amount of the less active Mg(OH)<sub>2</sub> in Ca/DM-600 and Ca/DM-700. It should be ascribed to the relatively low calcination temperatures (600–700 °C) of the parent dolomite that can decompose mainly MgCO<sub>3</sub> to MgO but unfavorably convert CaCO<sub>3</sub> to CaO, as indicated by the XRD results (Fig. 8). Leaching of the oxide species should be easier than that of the corresponding carbonates. Therefore, the phenomena occurring during the hydration of DM-600 and DM-700 can be expressed as the following equation below:

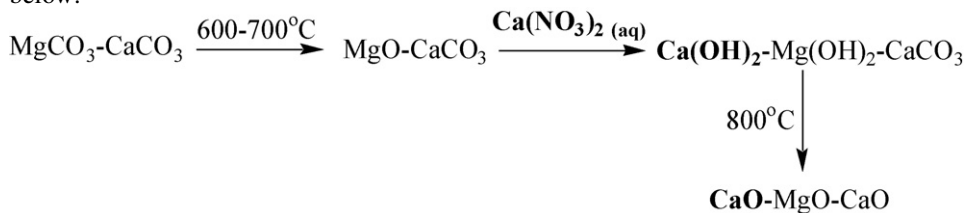


Interestingly, the high temperature DTG peaks of both Ca/DM-600 and Ca/DM-700 were separated into two peaks



with maxima at ca. 760 and 790 °C. The first peak should correspond to Mg(OH)<sub>2</sub> in the crystalline phase, while Ca(OH)<sub>2</sub> should be formed in smaller amounts on DM-600 and DM-700. In addition, the sharp and more intense DTG peaks observed at 766 °C, especially for Ca/DM-700, should indicate a formation of new crystalline hydroxide species. It was probably related to the Ca(OH)<sub>2</sub> precipitated from the Ca(NO<sub>3</sub>)<sub>2</sub> solution. The result implied that the Ca loaded was incorporated into the particles of DM-600 and DM-700 without the formation of the separate Ca(OH)<sub>2</sub> phase. Moreover, the total weight loss of both Ca/DM catalysts was comparable to that of the hydrated DM-800 (Fig. 10A), suggesting a small loss of surface area by the precipitation. It was confirmed by the N<sub>2</sub> adsorption–desorption measurement that Ca/DM-600 and Ca/DM-700 after calcined at 800 °C possessed surface areas of 34.1 and 33.4 m<sup>2</sup> g<sup>-1</sup>, respectively, slightly lower than that of DM-800 (36.4 m<sup>2</sup> g<sup>-1</sup>).

In the case of Ca/DM-600 and Ca/DM-700 (Fig. 10B and C), the peak at the highest temperature (790 °C) should be derived from the decomposition of CaCO<sub>3</sub> remaining in the parent dolomite after the calcination at 600–700 °C. An additional TGA experiment on pure CaCO<sub>3</sub> from limestone confirmed one step weight loss at 780 °C (not shown here). Therefore, after the final calcination of Ca/DM-600 and Ca/DM-700 at 800 °C, there should be at least two types of active basic sites mainly responsible for the transesterification. One is CaO generated from the precipitated Ca(OH)<sub>2</sub> located in the crystalline phase of dolomite and the other is highly basic CaO derived from CaCO<sub>3</sub> remaining in the parent dolomite itself. The formation of these two CaO sites can be expressed as the following equation below:



From the reaction and characterization results, it can be concluded that the high activity of Ca/DM-600 and Ca/DM-700 is due to the combination of two highly active CaO sites generated from the precipitated Ca(OH)<sub>2</sub> located in the crystalline phase of dolomite and from CaCO<sub>3</sub> remaining in the parent dolomite after calcined at 600–700 °C. When the parent dolomite was previously calcined at 800 °C, the highly active CaO derived from CaCO<sub>3</sub> was transformed to Ca(OH)<sub>2</sub> in the crystalline phase with small amount of separate Ca(OH)<sub>2</sub>. The CaO produced from the Ca(OH)<sub>2</sub> in the crystalline phase is believed to be the major catalytically active site in the modified dolomites. However, parts of this Ca(OH)<sub>2</sub> became inaccessible by the precipitated metal hydroxides covering the active surface of DM-800, resulting in the decreased transesterification activity. Under the present modification conditions, the metal oxides derived from the precipitate from corresponding nitrate salts were present as the minor phase, and catalyzed the reaction to some extent depending on their basic strength.

#### 4. Conclusions

The transesterification of PKO with methanol can be actively catalyzed over dolomite catalysts at 60 °C. Dolomite itself calcined at 800 °C (DM-800) was very active, giving the ME content of 96.1%, at the methanol/oil molar ratio of 50. The precipitation from nitrate salts of alkali earth metals and trivalent metals on DM-800 decreased the activity, and the basicity of DM-800, yielding lower methyl ester formation. However, among the metals used, Ca is the most active and suitable one. Changing the calcination temperature of the parent dolomite to 600 and 700 °C before the precipitation from Ca(NO<sub>3</sub>)<sub>2</sub>, and followed by the calcination at 800 °C (Ca/DM-600 and Ca/DM-700, respectively), gave a catalyst with very high activity, exhibiting the ME content as high as 99.9% at the methanol/oil molar ratio of 15. The suitable reaction conditions for the transesterification of PKO with methanol over Ca/DM-600 were the methanol/oil molar ratio of 15, the amount of catalyst of 10 wt.%, the reaction time of 3 h, and the temperature of 60 °C. Under these conditions, Ca/DM-600 catalyst can be repeatedly used three times, with the ME content higher than 95% maintained.

The TGA results suggested that the CaO generated from the precipitated Ca(OH)<sub>2</sub> located in the crystalline phase of dolomite and from CaCO<sub>3</sub> remaining in the parent dolomite itself was the catalytically active sites for the transesterification over Ca/DM-600 and Ca/DM-700, while the CaO derived from the accessible Ca(OH)<sub>2</sub> remaining in the crystalline phase of DM-800 after the modification was the major active site in the modified dolomite catalysts prepared from the parent dolomite calcined at 800 °C. The metal oxides formed by the

dehydroxylation of the precipitate of corresponding nitrate salts were present as the minor phase, and contribute the activity in the transesterification to some extent depending on their basic strength.

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