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Modification of calcite by hydration–dehydration method for heterogeneous biodiesel production process: The effects of water on properties and activity

Boonyawan Yoosuk*, Parncheewa Udomsap, Buppa Puttasawat, Pawnprapa Krasae

National Metal and Materials Technology Center (MTEC), 114 Thailand Science Park, Phahonyothin Road, Klong 1, Klong Luang, Pathumthani 12120, Thailand

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The study of solid basic catalyst is a promising route for developing a better understanding and contributes to the development of better heterogeneous catalytic system capable of carrying the transesterification of oils proficiently under mild reaction conditions in short reaction times. This paper reports a simple and flexible method for increasing the activity and improving the properties of calcined natural calcites via a hydration–dehydration approach in order to make them highly suitable for biodiesel production. The ensuing transformations of the calcite during synthesis were monitored by XRD, TPD, BET, and SEM techniques. The characterization results indicate that this synthesis offers a new calcium oxide with less crystallinity. The new CaO has higher surface area and amount of basic sites than CaO generated from the decomposition of calcite. The calcination of calcite changed the pore shape of catalyst but the water treatment did not alter the pore characteristics of CaO. With these characteristics, our CaO exhibits higher catalytic activity than the decomposed calcite as observed from the transesterification of palm olein with methanol. The methyl ester content was enhanced to 93.9 wt.% from 75.5 wt.% of calcined calcite. This present study also provides new fundamental insight into the effect of water on properties and activity of CaO prepared by new hydration and subsequent thermal decomposition method of calcined calcite.

1. Introduction

The transesterification process with the homogeneous base catalysts, NaOH, KOH, and $NaOCH_3$, has been used extensively in biodiesel production. However, these homogeneous catalysis systems have many drawbacks. Removing any of these catalysts from biodiesel fuel in order to purify it is difficult and requires a large amount of water. Consequently, a considerable amount of waste water is inevitably produced. Heterogeneous catalysis is an economically and ecologically important field in catalysis research because the catalysts have many advantages: they are non-corrosive and environmentally benign, and they present fewer disposal problems than do other catalysts. They are also much easier to separate from liquid products, and they can be designed to give higher activity, more selectivity, and longer catalyst lifetimes [1,2].

Many types of heterogeneous solid base catalysts, such as alkaline earth metal oxides and hydroxides, have been studied in regard to the transesterification of vegetable oils [1,3,4], various alkali metal compounds supported on alumina [5–7], zeolite [8], hydrotalcites [9], anion exchange resins [10] and polymer-supported guanidines [11]. The order of activity among alkaline earth oxide catalysts is BaO > SrO > CaO > MgO [9,12,13]. The active ingredients in most supported alkali catalysts, are easily corroded by methanol, and they exhibit short lifetimes. However, in most experiments using heterogeneous catalysts, the transesterification reaction proceeds at a relatively slow rate as compared to the transesterification reaction in those conducted with homogeneous catalysts. This typically slow reaction rate is due to diffusion problems accruing from the heterogeneous media's behavior as a three-phase system (oil/methanol/catalyst) [6]. Thus, the development of a solid basic catalyst capable of carrying the transesterification of oils proficiently under mild reaction conditions in short reaction times remains an intriguing and significant challenge.

In many areas of Thailand, calcite exists in natural abundance and has low toxicity. It is predominantly used in agriculture and cement manufacturing, and its main natural source is calcium carbonate with small amounts of silica, alumina, and ferrite. The catalytic application of calcite in many processes, such as gasification and reforming, has been the focus of much attention, as it is cheap, has high basicity, and is environmental friendly. However, few studies of its applications can be found in the literature, and in particular there is a dearth of studies on basic catalyzed chemical synthesis. Concerning biodiesel production, it has been reported that calcite has been used as a solid catalyst for transesterification. Suppes et al. [14] found that a rapeseed oil conversion of >95% can

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* Corresponding author. Tel.: +66 2564 6500; fax: +66 2564 6403.
E-mail addresses: boonyawy@mtec.or.th, yoosuk.b@gmail.com (B. Yoosuk).

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be achieved by using natural $CaCO_3$ rock when the reaction is carried out at 200 °C. It has been reported that its catalytic activity can be improved by employing thermal activation treatment such as calcinations (700 °C) in order to remove the surface carbonate and hydroxyl groups [15]. Upon a calcination at high temperature, the highly basic CaO is formed after the decomposition of carbonate groups in calcite.

Among the base catalysts, CaO is one of the most well-researched heterogeneous catalysts. Four reasons account for this: CaO has a higher basicity, lower solubility, and lower price than KOH/NaOH, and it is easier to handle. However, its transesterification reaction rate is still insufficient for practical applications. For example, Reddy et al. [16] produced nanocrystalline calcium oxides for biodiesel production at room temperature; yet, the reaction rate was slow, and 6–24 h were required to obtain a high conversion even with their most active catalysts. Yan et al. [17] reported a supported CaO catalyst with a methyl ester (ME) yield of 92% after 3.5 h. Although many studies have reported successfully using pure and/or modified CaO derived from the calcination of calcite as solid catalyst for biodiesel production, it is less efficient than liquid catalysts. This might be due to its low basicity and low surface area. Therefore, a higher catalyst weight and longer reaction time are needed, but both of these requirements result in high production costs.

The hydration and subsequent calcination method has reported to increase the surface area and bacisity of MgO [18] and hydrotalcites [19]. For the MgO, the transformation of MgO (periclase) to $Mg(OH)_2$ (brucite) and the reverse have been shown to occur simultaneously during catalyst preparation with changes in the textural and basic properties of the solid. During hydration, the brucite-like layers are reformed and the charge-compensating carbonate anions are replaced by hydroxyl anions that form Brønsted base sites. For the hydrotalcites, the decomposed-rehydrated Mg–Al hydrotalcite with Brønsted base sites was found to exhibit higher catalytic activity than the decomposed Mg–Al hydrotalcite with Lewis base sites [20,21].

In the present work, we propose the technique to improve the activity, basicity, and surface area of calcined natural calcite by using the hydration–dehydration method. The effects of water on the physical and chemical properties of calcined calcite with the use of various characterization techniques are reported here. We carried out the transesterification reaction of palm olein in order to examine the effects of water on the activity of catalysts.

2. Materials and methods

2.1. Material preparation

The calcite used in the study was from Saraburi Province, Thailand. The elemental composition analysis with an X-ray fluorescence (XRF) spectrometer indicated that the calcite was composed of CaO 97.20%, SiO_2 0.67%, Al_2O_3 0.29%, Fe_2O_3 0.28%, and CO_2 balance. Fresh calcite was thermally decomposed at 800 °C for 3 h. The solid product (CaO_S) was refluxed in water at 60 °C for 6 h, and the sample was filtered and heated at 120 °C overnight. Prior to use, the product, referred to as CaO_W, was subsequently dehydrated by heating at 600 °C for 3 h in order to change the hydroxide form to an oxide form, the latter being the active form for a transesterification reaction. The solid product was designated CaO_{600}. The commercially available CaO (CaO_C), purchased from Ajax Finechem, was used for comparison purposes. During the whole process, care was taken to minimize the exposure time of the catalysts to the atmosphere. All catalysts were used immediately after calcination process for the transesterification reaction of palm olein, thus limiting possible site contamination by CO_2 and water.

2.2. Material characterization

The X-ray diffraction (XRD) patterns were obtained on a JEOL JDX-3530 theta-2theta X-ray diffractometer with Cu Kα emission with 0.02° per step. The diffractograms were analyzed using the standard JCPDS files. Elemental analysis was performed on a Philips PW-2404 X-ray fluorescence spectrometer. Morphological study was carried out with an S-3400 Hitachi scanning electron microscope. The N_2 adsorption and desorption isotherms were measured on a Micromeritics ASAP 2020 instrument. Pore-size distributions of the samples were determined from the isotherms by the Barrett–Joyner–Hallenda (BJH) method. Fresh samples were dried before the adsorption measurement was taken.

Hammett indicator experiments were conducted to determine the H_- range of basic sites in each catalyst. The Hammett indicators used were bromothymol blue ($pK_a = 7.2$); phenolphthalein ($pK_a = 9.8$); indigo carmine ($pK_a = 12.2$); 2,4-dinitroaniline ($pK_a = 15.0$); and 4-nitroaniline ($pK_a = 18.4$). Although Hammett indicator measurements are usually performed in non-polar solvents, in this case anhydrous methanol was used in order to provide a more realistic assessment of base strength under transesterification conditions. 25 mg of catalyst was mixed with 4 ml of indicator solution, shaken, and allowed to sit for at least 2 h. The basic strength of the catalyst was taken to be higher than the weakest indicator that underwent a color change and lower than the strongest indicator that did not undergo a color change.

The basicity of catalyst was studied by temperature-programmed desorption (TPD) using CO_2 as a probe molecule. Prior to CO_2 adsorption, catalysts (0.3 g) were pretreated under a nitrogen stream at 120 °C for 30 min (10 °C/min and 20 ml/min). Then, the temperature was decreased down to room temperature, and a flow of pure CO_2 (20 ml/min) was subsequently introduced into the reactor for 150 min. The system was flushed with N_2 for 60 min. The TPD of CO_2 was carried out under a helium flow at a flow rate of 20 ml/min. The temperature was ramped from 40 to 960 °C and held at this temperature for 60 min with a temperature ramp of 10 °C/min. The CO_2 desorption was monitored by an online gas chromatograph provided with a thermal conductivity detector (TCD).

2.3. Catalytic activity for transesterification

The palm olein oil was purchased from Morakot Industries, PCL, Thailand. Its acid value is 1.10 mg of KOH/g. of oil. Purchased from Fluka, the methanol used in this study was of analytical reagent grade. The transesterification reaction was carried out in a batch reactor. A 200-ml round-bottom flask was equipped with a reflux condenser. The reaction temperature was controlled by a hotplate with temperature sensor, and the magnetic stirring rate of 500 rpm was adjusted (Heidolph).

The catalyst in the amount of 1.6 g (7 wt.% of catalyst based on oil weight) was mixed with 16.4 ml of methanol (methanol:oil molar ratio of 15:1). The mixture was warm at 60 °C. In addition, the 25 ml of palm olein oil also became warm at 60 °C, after which it was added to the mixture of methanol and catalyst. The mixture's temperature was kept at 60 °C by an oil bath. After the desired reaction time, the product of reaction was separated from the catalyst by centrifugation, and then the excess methanol was evaporated before the biodiesel yield was analyzed. The yield and compositions of the methyl ester products were determined by a gas chromatograph (GC-2010, Shimadzu) equipped with a capillary column, DB-WAX (30 m × 0.15 mm), and a flame ionization detector. The column temperature was programmed from 180 to 230 °C with the heating rate of 5 °C/min. Methylheptadecanoate was used as an internal standard for quantification. The percentage of methyl esters was calculated based on the standard method, EN 14103.

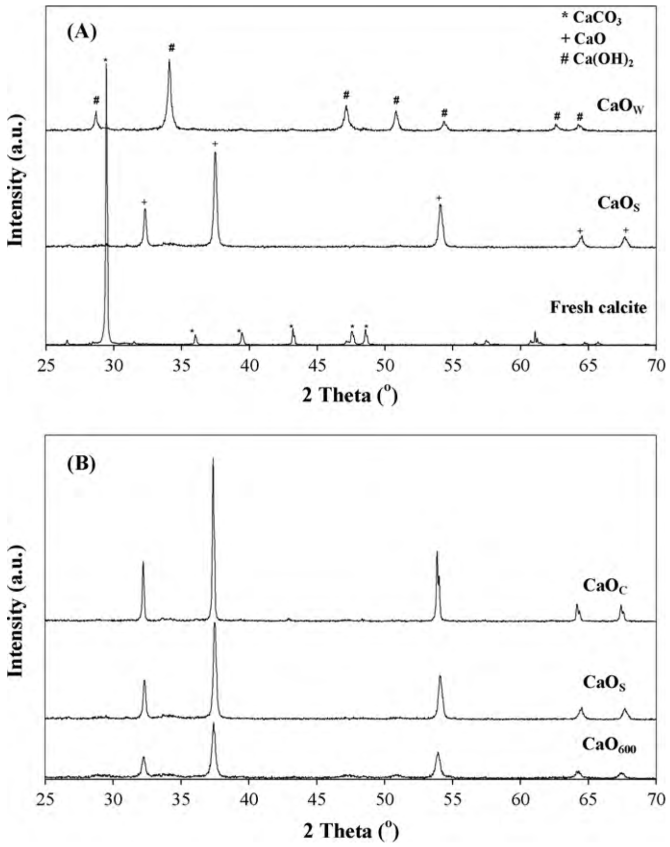

Fig. 1. XRD patterns of fresh calcite, CaO_S and CaO_W (A) and CaO_{600}, CaO_S and CaO_C (B). The peak intensity of fresh calcite was reduced 2.5 times.

Duplicate or triplicate experiments were performed and the average of duplicated tests is reported here. The errors for % ME content values were typically within ±2.0 wt.%.

3. Results and discussion

3.1. Characterization of catalysts

The crystallinity of all the samples was probed by powder XRD. The diffraction pattern for commercially available CaO (CaO_C) was also presented for comparison purposes. Fig. 1A shows the XRD patterns for fresh calcite, CaO_S, and CaO_W. The parent material showed major diffraction peaks at 29.4°, 36.2°, and 47.5°, which is characteristic of $CaCO_3$ (calcite). Following calcination, the reflections arising from the calcite were lost, coincident with the appearance of new crystalline phases that can be assigned to highly crystalline CaO (32.2°, 37.4°, and 53.9°). Peak width analysis using Scherrer's equation [22] revealed the nanocrystalline nature of the new phases, with an average crystalline size of 55.5 nm (Table 1). After the CaO_S had been hydrated, the most immediate inference is that the surface hydration proceeded deeply into the bulk, turning all the calcium oxide into calcium hydroxide with a lower degree of crystallinity than that of commercial $Ca(OH)_2$ (not present here).

Fig. 1B shows the diffraction patterns of the solids, CaO_S and CaO_{600}. It also shows the diffraction pattern of commercial CaO for comparison purposes. The CaO_C showed a very high degree of crystallinity with a crystalline size of more than 100 nm. As compared to commercial CaO, both CaO_S and CaO_{600} exhibited a weak XRD peak, indicating a poorly crystalline structure that is characteristic of calcium oxide. The intensity of the peaks decreased significantly when the CaO_S was hydrated and subsequently calcined. As can be seen, no crystal phase other than that of the CaO was produced by the hydration with water. The crystallized size (Table 1) also shows that the nanocrytalline CaO with a particle size of 42.2 nm was generated by the hydration followed by thermal dehydration of the calcined natural calcite. It is smaller than that obtained by CaO from the calcination of natural calcite. The XRD results indicate that crystallinity and crystalline size of catalyst was significantly affected by the water treatment. Both decreased considerably. This phenomenon has also been demonstrated previously in hydrotalcite-like compounds [23] and MgO [18].

Natural calcite has a very small surface area and negligible basicity, as shown in Table 1. Calcination at 800 °C changes both the structural and chemical properties of calcite, as evidenced by an increased surface area and increased basic strength. This result should be due to the expulsion of CO_2 from carbonate-rich areas that generate higher porous material. An attempt was made to increase the solid surface area by hydration followed by use of the thermal decomposition technique. This technique yielded solid CaO_{600} with a surface area twice that of the CaO_S. This is likely associated with the evolution of H_2O, whose expulsion from the lattice during the calcination of CaO_W would be expected to fracture the crystallites, with the concomitant formation of extra base sites in CaO_{600}. Additional, CaO_S and CaO_{600} showed greater surface area and stronger basic strength than commercial CaO.

Nitrogen adsorption/desorption isotherms for fresh calcite, CaO_S and CaO_{600} are shown in Fig. 2. All samples exhibit type IV isotherms characteristic of mesoporous materials [24]. The hysteresis loop is small and possesses features reminiscent of both the H3 and H1 type (IUPAC classification). Fresh calcite showed the shape of hysteresis loop corresponds to H3-type for slit shaped mesopores. The adsorption appears to be limiting at high P/P_0 in case of CaO_S and CaO_{600}, suggests that the latter classification is a more valid description. Type H1 hysteresis is usually associated with solids consisting of nearly cylindrical channels or agglomerates or compacts of near uniform spheres. As can be seen in Fig. 2, the hysteresis loop is narrow, with almost parallel adsorption and desorption branches. This is indicative of pores with regular geometry. The isotherm results reveal that the calcination at 800 °C of calcite changes the pore shape from H3 to H1. On the other hand, the pore characteristics were not changed significantly after the water treatment although both surface area and pore volume increased intensively.

The surface morphologies of the fresh calcite, CaO_S, and CaO_{600} were examined by SEM as shown in Fig. 3. The SEM results support the XRD results showing that the fresh calcite exhibited large particles with smooth planes and a high degree of crystallinity. Cal-

Table 1
Properties of fresh calcite and its derived samples compared with commercial CaO.

Properties/samples	Fresh calcite	CaO_S	CaO_{600}	CaO_C[a]
Surface area (m^2/g)	0.4	12.4	25.0	2.1
Pore volume (cm^3/g)	0.01	0.19	0.25	0.02
Crystalline size (nm)	>100.0	55.5	42.2	>100.0
Basic strength (H_-)	$H_- < 7.2$	$12.2 < H_- < 15.0$	$12.2 < H_- < 15.0$	$9.8 < H_- < 12.2$

[a] Commercial available CaO.

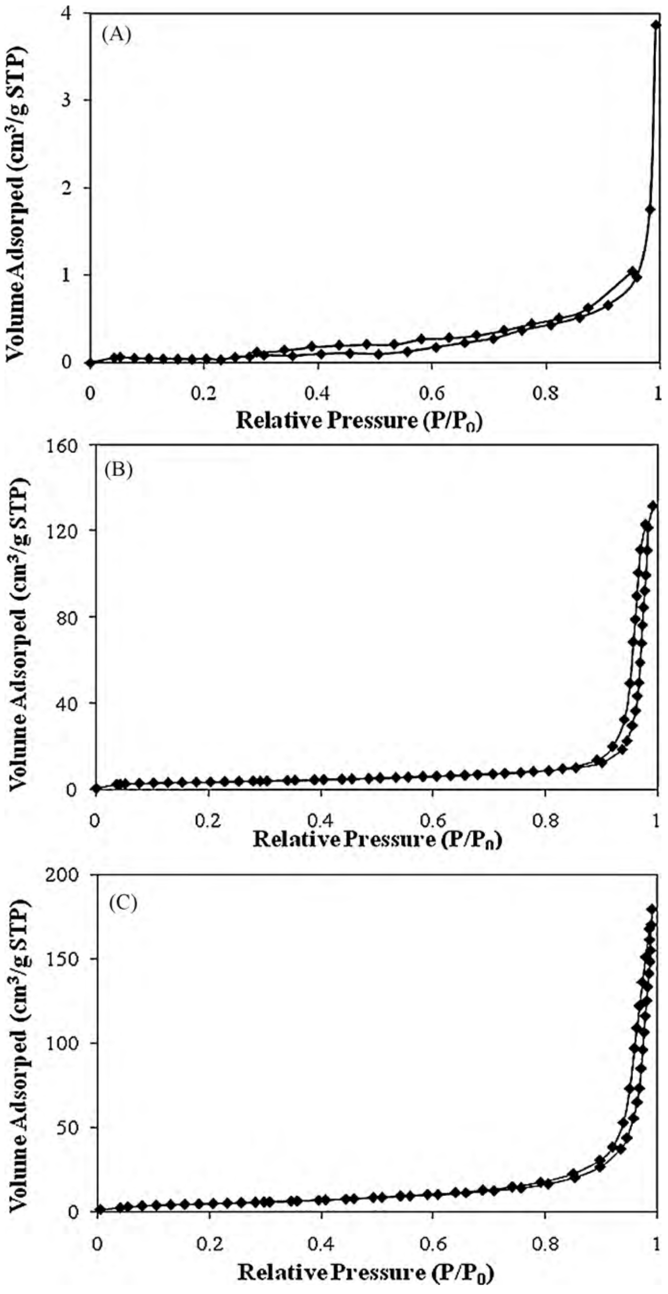

Fig. 2. N_2 adsorption/desorption isotherms of fresh calcite (A), CaO_S (B) and CaO_{600} (C).

cination at 800 °C changed these surfaces, making them rougher and decreasing the particle size. After hydration and subsequent calcination at 600 °C, the highly textured, that is, very rough, surface was revealed. However, there is no any important change observed. All results indicate that this procedure considerably improved the chemical properties of the resulting solid.

The basicity of all the samples was measured by temperature-programmed desorption of CO_2. The transesterification activity depends on the number of basic sites present in the catalysts as well as on their strength. The TPD measument of CaO_C was did for comparison purposes. The results of CO_2 TPD measurements on CaO_{600}, CaO_S, and CaO_C were summarized in Table 2. CaO_{600} and CaO_S showed the desorption peak in the same temperature range (656–960 °C) while the desorption peak belong to CaO_C was in the lower temperature range (609–876 °C). These TPD results agree very well with the order of basic strength obtained by Hammett indicator experiments (Table 1) showing that the basic sites of CaO_{600} and CaOs were stronger than that of CaO_C. Additional, the desorption peak was present at a very high temperature for all the samples. This might be due to the presence of much stronger basic sites, i.e., super basic sites.

From Table 2, it is apparent that the calcined calcite shows a high number of total basic sites as compared to the commercial CaO. After hydration and subsequent thermal dehydration at 600 °C, CaO_{600} possesses the highest concentration of strong basic sites. From the results, the amount of total basicity varied in the order of $CaO_{600} > CaO_S > CaO_C$. These results are consistent with the previous results reported by Aramendia et al. [25]. A comparison of surface basic site density, defined as the number of micromoles of CO_2 chemisorbed per square meter of surface area, reveals that treatment with water produced a solid over three times more basic and with a higher basic site density than the CaO obtained from the calcination of calcite. The information provided by TPD technique can be concluded that the active sites produced by the calcination of the hydrated sample at 600 °C have higher basicity than those generated from calcinations of fresh calcite at 800 °C. The phenomenon that occurred during the catalyst synthesis could be as shown by Eqs. (1)–(3).

$$\text{Natural calcite} \xrightarrow{800\,^{\circ}\mathrm{C}} \mathrm{CaO} + \mathrm{CO_2} \tag{1}$$

$$\mathrm{CaO} + \mathrm{H_2O} \xrightarrow{60\,^{\circ}\mathrm{C}} \mathrm{Ca(OH)_2} \tag{2}$$

$$\mathrm{Ca(OH)_2} \xrightarrow{600\,^{\circ}\mathrm{C}} \text{highly basic-CaO} + \mathrm{H_2O} \tag{3}$$

Therefore, all characterization results indicate that the hydration–dehydration of calcined calcite is a sufficient technique for generating a new calcium oxide with excellent chemical textural properties and a large number of basic sites. This new calcium oxide, therefore, will be highly suitable for use as a heterogeneous catalyst in biodiesel production.

3.2. Transesterification of palm olein with methanol

The catalytic activities of all samples were subsequently examined by the transesterification of palm olein with methanol. Fig. 4 graphically illustrates the evolution of the ME content for a series of fresh calcite and its derived samples compared with commercial CaO. No methyl ester was observed when fresh calcite was used. This suggests that the basicity of the carbonate form of calcium is not high enough to catalyze the transesterification reaction. After the calcination of the fresh calcite at 800 °C, the activity of the catalyst increased significantly. Within 1 h, 75.5 wt.% of ME content had been obtained. The hydration without further calcination (CaO_W) decreased the activity of the catalyst from 75.5 to 3.5 wt.% of ME content. This might be due to the fact that, for alkaline earth metal, the oxide form has stronger basicity than does the hydroxide form. However, CaO_W showed higher activity than the fresh calcite did. These activity results are consistent with the order of basic strength, as shown in Table 1: $CaO_S > CaO_W >$ fresh calcite. The basic strength of CaO_W in this study was $9.8 < H_- < 12.2$.

From Fig. 4, the greatest catalytic activity was observed for CaO_{600}. 93.9 wt.% of ME content was obtained at the reaction time of 1 h. The CaO_{600} processed 18.4 wt.% ME content higher than CaO_S. The commercial CaO showed less activity than both CaO_S and CaO_{600}. It is clear that the hydration and subsequent thermal decomposition of the calcined calcite is essential in order to get an active catalyst for this kind of reaction. The finding correlates to the results of the CO_2 TPD measurements, showing greater number of strong basic sites for CaO_{600} as compare to both CaO_S and CaO_C. This confirms the knowledge that the activity of catalysts in the transesterication strongly depends on their basicity. Thus, the high activity of CaO_{600} could be due to the presence of a high total

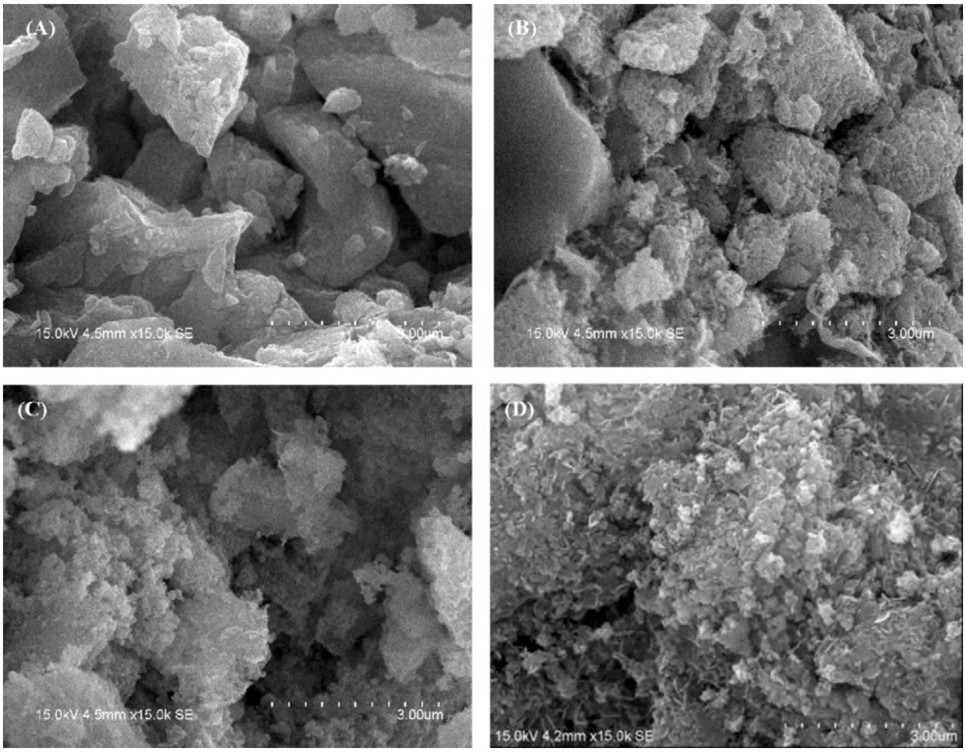

Fig. 3. SEM images of fresh calcite (A), CaO_S (B), CaO_{600} (C) and used CaO_{600} (D).

Table 2
Results of CO_2 TPD measurements on CaO_S, CaO_{600} and CaO_C.

Samples	Temperature range (°C)	Total basicity (μmol of CO_2/g)	Basic site density[a] (μmol of CO_2/m^2)
CaO_S	656–960	505.7	40.8
CaO_{600}	656–960	1532.4	61.3
CaO_C[b]	609–876	64.1	30.5

[a] Basic site density = total basicity of sample (μmol/g(cat))/specific surface area of sample (m^2/g(cat)).

[b] Commercial available CaO.

number of basic sites as compared to its counterparts. The study on the transesterification reaction indicates that the reconstruction of decomposed calcite by hydrating subsequent calcinations generates highly active CaO. During catalyst preparation, the carbonates have been decomposed and then the so formed Ca oxide is hydrated, thus forming Brønsted base sites. The decomposed-hydrated calcined calcite with Brønsted base sites exhibited higher catalytic activity than the decomposed calcite for the transesterification reaction of the triglyceride with methanol.

The optimum reaction time for the transesterification over CaO_{600} was determined by performing reactions at varying reaction times in the range of 15–90 min. Fig. 5 shows the dependence of the ME content on the reaction time over CaO_{600}. The results show that the ME content significantly increased from 0 to 30 min. After that, it gradually improved and reached the maximum at the reaction time of 45 min, giving an ME content of 95.7 wt.%. However, after the reaction time had been prolonged to 90 min, it was found that the ME content had slightly decreased. This may be due to the reverse transesterification reaction. These results indicate that the reaction time required to obtain the highest amount of methyl esters is 45 min.

As a comparison, KOH catalyst was tested as commonly used homogeneous catalyst and the reaction was carried out using 1.0 wt.% catalyst by weight of oil and methanol:oil molar ratio of 6:1. The results, illustrated in Fig. 5, indicate that the homogeneous catalysts proceed much faster than heterogeneous catalysts in transesterification of vegetable oils to biodiesel. This difference may be due to the diffusion problems accruing from the heterogeneous media's behavior as a three-phase system (oil/methanol/catalyst). Another reason can be that KOH is soluble in methanol. Almost all KOH added in the homogeneous process react with methanol and form potassium methoxide whereas the amount of active species formed in the heterogeneous reaction depends critically on the surface properties and texture of the solid catalysts.

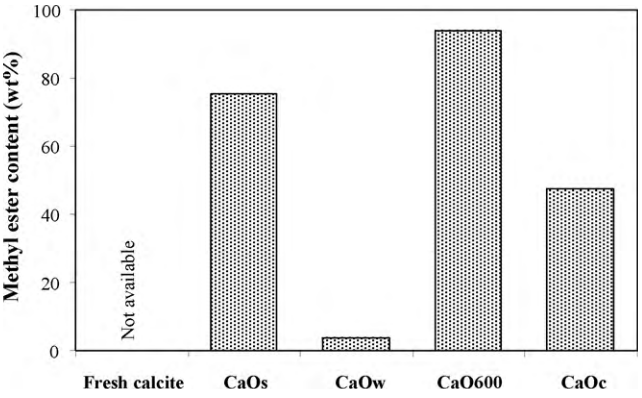

Fig. 4. Methyl ester content obtained over fresh calcite and its derived samples. Reaction conditions: methanol/oil molar ratio, 15; catalyst weight, 7 wt.%; time, 60 min; temperature, 60 °C (CaO_C represents commercial CaO).

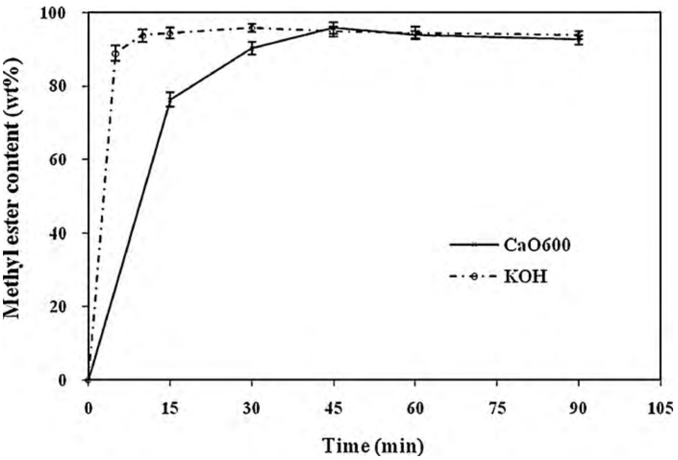

Fig. 5. Dependence of methyl ester content on the reaction time over CaO_{600} and KOH at temperature of 60 °C. Reaction conditions for CaO_{600}: methanol/oil molar ratio, 15 and catalyst weight, 7 wt.%. Reaction conditions for KOH: methanol/oil molar ratio, 6 and catalyst weight, 1 wt.%.

In the heterogeneous catalysis system, the reaction mixture consists of three phases (oil/methanol/catalyst). The active methoxide species is formed upon adsorption of methanol on the catalyst surface, and the transesterification reaction becomes mass-transfer controlled [6]. Knowledge of the kinetics of how heterogeneous catalysts affect transesterification is very limited at the moment. However, it has been reported that, in the presence of solid base catalysts, the reaction involves the active participation of methoxide species, and then, the efficiency of the catalyst should be related with the rate of formation of methoxide anion [26]. Dossin et al. [4] studied the kinetics of the transesterification of ethyl acetate with methanol by using MgO as a catalyst. They found that methanol adsorption was the rate-determining step. This is in contrast with the use of KOH (methanol soluble) as a catalyst, for which the reaction mixture is a two-phase oil:methanol system wherein the amount of methanol has little effect on the formation of the methoxide species. In this case, the initial transesterification rate is determined by the concentration of KOH in the methanol phase [27].

However, the use of homogeneous base catalysts requires neutralization and separation from the reaction mixture leading to a series of environmental problems related to the use of high amounts of solvents and energy. Heterogeneous solid base catalysts can be easily separated from the reaction mixture with the use of less amount of water, they are easily regenerated and have a less corrosive nature, leading to safer, cheaper and more environment-friendly operations.

Reusability is one of the most important features for a heterogeneous catalyst that is to be used commercially. Thus, the reusability of CaO_{600} was examined by carrying out subsequent reaction cycles. After each cycle, reaction mixtures were carefully withdrawn, the catalyst sediment recovered, and a new reaction cycle started with fresh reactants. The collected catalysts were used directly without re-calcination. During the whole process, care was taken to minimize the exposure time of the catalysts to the atmosphere, thus limiting possible site contamination by CO_2.

Fig. 3C and D shows the SEM images of fresh and used CaO_{600} catalysts, respectively. The SEM analysis revealed a similar morphology. A major change was not observed. Fig. 6 shows the reusability of the CaO_{600} catalyst in the transesterification of palm olein. It was revealed that the collected catalyst was not as active as the fresh one. The CaO_{600} maintained sustained activity even after being used for 5 cycles. However, a slightly lowered level of activity was found after the second repetition. This decrease in activity may be due to the active site blockage by adsorbed intermediates or product species, such as diglyceride, monoglyceride, and glycerol, and contamination by O_2, H_2O, and CO_2 in the air during the process. The leaching of active species into the reaction mixture also contributes to the reduced activity level.

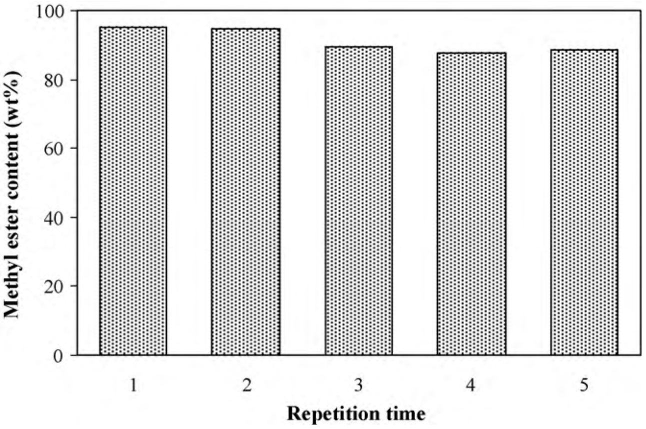

Fig. 6. Reusability of CaO_{600} in the transesterification of palm olein. Reaction conditions: methanol/oil molar ratio, 15; catalyst weight, 7 wt.%; time, 60 min; temperature, 60 °C.

For basic oxides, metal ion leaching into solution is always a primary concern directly affecting catalyst deactivation characteristics. The elemental analysis of the mixture after reaction using atomic absorption spectroscopy (AAS) showed that there is the amount of metal fraction that remained in reaction mixture. The data shows that 0.456 mg of CaO ml^{-1} was dissolved into biodiesel phase while the amount of Ca in the glycerol–methanol phase was equivalent to 0.975 mg of CaO per ml of final alcoholic phase. This result indicated that the catalyst has lost some active species during the transesterification process which is one of the factors cause the reduction of activity.

It has been reported that CaO dissolves slightly in the reaction media as it is soluble to some extent in methanol (0.035 wt.%) [1]. Granados et al. [15] showed that the transesterification over CaO is the result of the heterogeneous and homogeneous contributions. Part of the reaction takes place on basic sites at the surface of the catalyst, the rest is due to the dissolution of the activated CaO in methanol, which creates homogeneous leached active species. However, the dissolution of the CaO in the reaction media is not as intense as to result in the decline in catalytic performance while using the solid for many runs as long as a sufficient amount of solid catalyst is initially loaded.

Some studies have also demonstrated that CaO can be reused for several runs [16,28,29]. This indicates the possibility of using CaO as a catalyst for biodiesel production. Although the heterogeneous process based on CaO is still less active than the NaOH or KOH homogeneous process, on either a weight or molar basis, this difference can be overcome using larger initial CaO loading as long as the CaO can be reused for a greater number of runs. In addition, although the CaO_{600} catalyst cannot be reused many times, calcite is naturally abundant and can be found in many areas of Thailand. It is also very inexpensive. Moreover, the present method for calcite modification is not complicated and is, therefore, easy to carry out. Hence, there is potential for further developing calcite for commercial scale biodiesel production.

4. Conclusions

The present study show that hydration and subsequent thermal decomposition is a sufficient method to increase the activity of calcined natural calcite and contributes to the development of better heterogeneous catalysts for biodiesel production. This technique generates a new calcium oxide with excellent textural properties and a large number of basic sites. Crystallinity and crystalline size of catalyst was significantly decreased by the water treatment as suggested from XRD. The SEM images agree very well with the BET results showing that the surface area of the catalyst can be enhanced by this method. The highly textured, that is, very rough, surface was also revealed for the resulting solid, which is associated with the expulsion of CO_2 and H_2O from the lattice. The calcination of calcite changed the pore shape of catalyst but the water treatment did not alter the pore characteristics of CaO although both surface area and pore volume increased intensively. The desorption profile showed the presence of numerous strong basic sites in the catalysts obtained by this method. During catalyst preparation, the carbonates have been decomposed and then the so formed Ca oxide is hydrated, therefore, forming Brønsted base sites. The decomposed-hydrated calcined calcite exhibits a higher catalytic activity than the decomposed natural calcite does, as shown in the results of the palm olein transesterification with methanol. The ME content was enhanced 18.4 wt.%. This is due to the presence of higher basicity and a larger surface area than its counterparts. The ME content as high as 95.7 wt.% can be obtained over CaO_{600} under suitable conditions, that is, with a methanol/oil molar ratio of 15, a catalyst weight of 7 wt.%, a reaction temperature of 60 °C, and a reaction time of 45 min.

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