Chemical Engineering Journal 145 (2009) 468–474

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Al_2O_3-supported alkali and alkali earth metal oxides for transesterification of palm kernel oil and coconut oil

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ARTICLE INFO

Article history:
Received 2 November 2006
Received in revised form 19 April 2008
Accepted 28 April 2008

Keywords:
Biodiesel
Transesterification
Heterogeneous catalysts

ABSTRACT

Transesterification of palm kernel oil (PKO) and coconut oil (CCO) with methanol was investigated under a heterogeneous catalysis system. Various Al_2O_3-supported alkali and alkali earth metal oxides prepared via an impregnation method were applied as solid catalysts. The supported alkali metal catalysts, $LiNO_3/Al_2O_3$, $NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3, with active metal oxides formed at calcination temperatures of 450–550 °C, showed very high methyl ester (ME) content (>93%). XRF analysis suggests this is likely to be due to a homogeneous catalysis of dissoluted alkali oxides. On the other hand, $Ca(NO_3)_2/Al_2O_3$ calcined at 450 °C yielded the ME content as high as 94% with only a small loss of active oxides from the catalyst, whereas calcined $Mg(NO_3)_2/Al_2O_3$ catalyst possessed an inactive magnesium-aluminate phase, resulting in very low ME formation. At calcination temperatures of >650 °C, alkali metal- and alkali earth metal-aluminate compounds were formed. Whilst the water-soluble alkali metal aluminates formed over $NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3 were catalytically active, the aluminate compounds on $LiNO_3/Al_2O_3$ and $Ca(NO_3)_2/Al_2O_3$ are less soluble, giving very low ME content. The suitable conditions for heterogeneously catalyzed transesterification of PKO and CCO over $Ca(NO_3)_2/Al_2O_3$ are the methanol/oil molar ratio of 65, temperature of 60 °C and reaction time of 3 h, with 10 and 15–20% (w/w) catalyst to oil ratio for PKO and CCO, respectively. Some important physical and fuel properties of the resultant biodiesel products meet the standards of diesel fuel and biodiesel issued by Department of Energy Business, Ministry of Energy, Thailand.

1. Introduction

Biodiesel is mono-alkyl esters of fatty acids derived from vegetable oils and animal fats. It has received increasing levels of attention as a potential alternative green fuel due to its non-toxic, sulfur- and aromatic-free, biodegradable and renewable material status [1]. The physical and fuel properties, i.e. kinematic viscosity, specific gravity, calorific value, flash point, and cetane number of biodiesel are categorized into the same range as that of petroleum-based diesel fuel. Thus, it can be applied to the mass of currently existing compression-ignition diesel engines with little or no modifications. The additional advantage is that, like any other biomass-derived fuels, the exhaust gas from biodiesel combustion contains no SO_x and a relatively small amount of CO, unburnt hydrocarbons and particulate matter, compared to the combustion of conventional diesel fuel [2–4].

Conventional biodiesel production is performed through the transesterification of triglycerides from vegetable oils and animal fats with mono-alkyl alcohols, for example methanol and ethanol. The process is usually carried out in the presence of a homogeneous base or acid catalyst to reduce the reaction temperature and to control the product selectivity. Sodium or potassium hydroxides, carbonates or alkoxides are the common base catalysts [5–8] and the often used acid catalysts are sulfuric and hydrochloric acids [9–11]. However, these homogeneous catalysis systems have many drawbacks. Removal of the catalysts to purify the biodiesel fuel and glycerol 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 relating to the development of heterogeneous catalysts for transesterification of various oils with methanol have been reported [12–16]. Natural calcium carbonate rock is a cheap catalyst but its activity is low and a high reaction temperature is required to achieve the conversion of >95% [12]. On the other hand, Kim et al. [13] applied $Na/NaOH/\gamma\text{-}Al_2O_3$ as a strong base catalyst to the transesterification of soybean oil, showing a comparable performance to the conventional homogeneous NaOH catalyst. Al_2O_3-supported potassium oxides derived from carbonate [14], nitrate [15] and iodide [16] salts of potassium are also catalytically active, giving a high triglyceride conversion. However, the catalysis over these supported alkali metal oxides has been con-

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doi:10.1016/j.cej.2008.04.036

sidered to occur through the homogeneous route to a significant extent [17], since the oxides of alkali metal group are generally water-soluble [18]. Consequently, the major drawbacks of homogeneous catalysis are not be technically resolved by using these types of catalysts. In contrast, oxides of alkali earth metals are less soluble in methanol [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.

In the present work, we studied the transesterification of palm kernel oil and coconut oil, which are readily available at a relatively low price in Thailand, using various Al_2O_3-supported alkali and alkali earth metal oxides prepared through the conventional impregnation method as catalysts. Effects of metal types, calcination temperatures, and reaction conditions were investigated together with a combination of structural characterization and elemental analysis. Under suitable catalyst preparation and transesterification conditions, biodiesel products with the methyl ester purity of 94% could be obtained. Some important fuel properties of the biodiesel produced were compared with the standard range of diesel fuel and biodiesel specifications issued by Department of Energy Business, Ministry of Energy, Thailand.

2. Experimental

2.1. Catalyst preparation

Supported metal oxide catalysts were prepared according to the conventional incipient-wetness impregnation of aqueous solutions of the corresponding metal salt precursors on an aluminum oxide support. The metal precursors applied to the study were analytical grade nitrate salts of alkali and alkali earth metals, including $LiNO_3$, $NaNO_3$, KNO_3, $Mg(NO_3)_2{\cdot}6H_2O$, and $Ca(NO_3)_2{\cdot}4H_2O$ (Ajax Chemicals). Al_2O_3 support (Fluka) has a BET surface area of 126 $m^2\,g^{-1}$. It was calcined at 450 °C for 2 h before being used. Typically, a required amount of metal nitrate salt was completely dissolved in deionized water at ambient temperature. The support was then added into the solution followed by vigorous mixing. The amount of metal loading was maintained at 20 $mmol_{metal}\,g^{-1}_{support}$. After equilibrating the mixture for 2 h, the paste was dried in an oven at 120 °C overnight. Prior to use in the transesterification, the dried solid was calcined at 450–850 °C for 4 h.

2.2. Transesterification reaction procedure

Refined palm kernel oil (PKO) was donated by Chumporn Palm Oil Industry Co. Ltd. Refined coconut oil (CCO) is a commercial grade. Both were used as received. The fatty acid composition and physicochemical properties of the oils are summerized in Tables 1 and 2, respectively. The reaction was carried out in a 250-mL three-neck round bottom flask equipped with a condenser and a magnetic stirrer. Typically, 1 g of calcined catalyst was suspended in a required volume of methanol (99.5%, commercial grade) and heated to a controlled temperature of 60 °C by a water bath. Subsequently, the oil was added into the mixture under vigorous stirring. The methanol/oil molar ratios were varied between 10 and 65. 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. Methyl ester product was recovered in a separating funnel, followed by washing with deionized water and drying with anhydrous Na_2SO_4.

Composition of methyl esters produced was analyzed with a Varian CP-3800 gas chromatograph (GC) equipped with a FID detector and a 30-m DB-1 capillary column. Methyl ester (ME) content was calculated based on the internal standard method using *n*-decane as a reference. The accuracy of this method was confirmed by comparing the data with those obtained according to the standard method of EN 14103.

Table 1
Fatty acid composition of palm kernel and coconut oils used in the present study

Fatty acid	Fatty acid composition (wt.%)	
	Palm kernel oil	Coconut oil
C 6:0 Caproic acid	0.24	0.50
C 8:0 Capryric acid	5.14	9.95
C 10:0 Capric acid	4.82	7.90
C 12:0 Lauric acid	59.83	51.00
C 14:0 Myristic acid	14.92	16.46
C 16:0 Palmitic acid	5.38	6.09
C 18:0 Stearic acid	1.52	1.90
Saturated	91.85	93.80
C 18:1 Oleic acid	6.87	4.94
C 18:2 Linoleic acid	1.28	0.82
Unsaturated	8.15	5.76
Total fatty acid	100	100
Average molecular weight	677	659

2.3. Catalyst characterization

Crystallinity of supports and metal oxide catalysts was confirmed by technique of powder X-ray diffraction (XRD) using a Rigaku D/MAX 2200/Ultima + diffractometer. Elemental analysis was performed on an ED-2000 energy dispersive X-ray fluorescence (XRF) spectrometer. N_2 adsorption–desorption was measured on a Micromeritics ASAP 2020 surface area and porosity analyzer to characterize BET surface area and textural properties of catalysts.

3. Results and discussion

As shown in Tables 1 and 2, the fatty acid composition of the refined PKO and CCO used here was similar, mainly consisting of lauric acid (C_{12}), and the water content was very low. This is an advantage to avoid dissolution of active metal oxides into water, and poisoning of basic sites by water molecules. Thus, the interpretation of catalytic results is less complicated. However, it can be seen that CCO has a significantly higher acid value than PKO (Table 2). This difference may contribute to a variation in the reaction conditions required for the heterogeneously catalyzed transesterification of each of the two oils. Moreover, the acidity of free fatty acids can be harmful to basic sites through the acid–base neutralization [20].

3.1. Effect of active metal components

Table 3 shows the ME contents obtained from various Al_2O_3 supported metal oxide catalysts after being calcined at 450 °C. The transesterification reaction of PKO was carried out at 60 °C for 3 h

Table 2
Physicochemical properties of palm kernel and coconut oils used in the present study

Properties	Analysis results	
	Palm kernel oil	Coconut oil
Density at 15 °C (g^{-1} mL)	0.922	0.920
Kinematic viscosity at 40 °C ($mm^2\,s^{-1}$)	28.52	27.96
Acid value ($mg_{KOH}\,g_{oil}^{-1}$)	2.49	11.59
Moisture content (wt.%)	0.1	0.19
Iodine value (g_{iodine} 100 g_{oil}^{-1})	17.55	8.35

Table 3
Methyl ester (ME) content of the biodiesel from transesterification[a] of palm kernel oil over supported metal oxides calcined at 450 °C

Catalyst	ME content (wt.%)
Al_2O_3	0
$LiNO_3/Al_2O_3$	91.6
$NaNO_3/Al_2O_3$	24.7
KNO_3/Al_2O_3	34.5
$Mg(NO_3)_2/Al_2O_3$	10.4
$Ca(NO_3)_2/Al_2O_3$	94.3
CaO	38.5
$Ca(OH)_2$	5.7
$CaCO_3$	3.4

[a] Reaction conditions: methanol/oil molar ratio, 65; catalyst amount, 10 wt.% based on oil weight; temperature, 60 °C; time, 3 h.

Table 4
Methyl ester (ME) content of the biodiesel from transesterification[a] of palm kernel oil over supported metal oxides calcined at various temperatures

Catalyst	Calcination temperature (°C)	ME content (wt.%)
$LiNO_3/Al_2O_3$	450	91.6
	550	93.4
	650	76.6
	850	4.1
$NaNO_3/Al_2O_3$	450	24.7
	550	93.8
	650	95.1
	850	94.7
KNO_3/Al_2O_3	450	34.5
	550	94.7
	650	86.3
	850	54.4
$Mg(NO_3)_2/Al_2O_3$	450	10.4
	550	3.8
	650	2.4
	850	1.5
$Ca(NO_3)_2/Al_2O_3$	450	94.3
	550	21.7
	650	3.5
	850	3.6

[a] Reaction conditions: methanol/oil molar ratio, 65; catalyst amount, 10 wt.% based on oil weight; temperature, 60 °C; time, 3 h.

with the methanol/oil ratio of 65. In all experiments, there was no formation of soap. Calcined Al_2O_3 itself did not contribute to the formation of ME. However, the impregnation of alkali and alkali earth metals enhanced the ME content. It can be seen that $LiNO_3/Al_2O_3$ and $Ca(NO_3)_2/Al_2O_3$, giving the ME contents >90%, catalyzed the PKO transesterification much more actively than $NaNO_3/Al_2O_3$, KNO_3/Al_2O_3 and $Mg(NO_3)_2/Al_2O_3$ under these conditions. These results are unexpected since the oxides of Na and K are commonly more basic than alkali earth oxides.

To identify the presence of the metal oxide species, XRD analyses of the catalysts after treating at 450 °C were performed. As illustrated in Fig. 1, over $LiNO_3/Al_2O_3$ and $Ca(NO_3)_2/Al_2O_3$ catalysts, most of the corresponding metal nitrate precursors were decomposed with the concomitant formation of mainly the metal oxides and metal-aluminate compounds. In contrast, many diffraction peaks related to the nitrate salts still remained on the catalysts using $NaNO_3$ and KNO_3 as the precursors. This observation suggests that the calcination of $NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3 at 450 °C did not sufficiently convert the corresponding nitrate precursors into the active oxide forms, thus resulting in the low ME contents.

Although CaO species were mainly formed after the calcination of $Ca(NO_3)_2/Al_2O_3$ catalyst at 450 °C, they were considered to have a different nature to bulk CaO. As shown in Table 3, $Ca(NO_3)_2/Al_2O_3$ was much more active than CaO, $Ca(OH)_2$ and $CaCO_3$ under the same calcination conditions. Small crystalline CaO particles formed through a suitable impregnation method may be more basic and active than bulk CaO. A synergetic effect between active metal oxides and supports or within metal oxide particles has also been suggested for many heterogeneously acid–base catalyzed reactions [21,22].

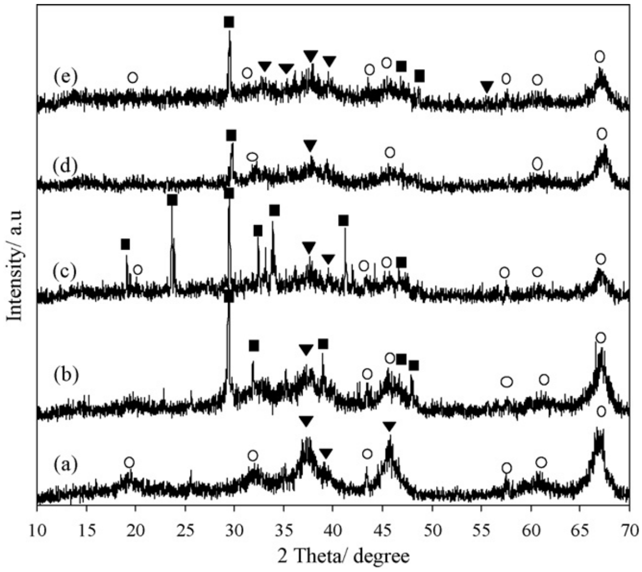

Fig. 1. XRD patterns of Al_2O_3-supported metal oxide catalysts after calcination at 450 °C: $LiNO_3/Al_2O_3$ (a), $NaNO_3/Al_2O_3$ (b), KNO_3/Al_2O_3 (c), $Mg(NO_3)_2/Al_2O_3$ (d), and $Ca(NO_3)_2/Al_2O_3$ (e). (Symbols: (■) nitrate salts, (▼) metal oxides, and (○) Al_2O_3).

In the case of $Mg(NO_3)_2/Al_2O_3$, although a small number of peaks related to the residual nitrate salt were found, we did not observe peaks of magnesium oxide. Moreover, the characteristic peaks of the alumina support ($2\theta = 19.8°, 32°, 37.5°, 46°, 57.4°, 60.7°$ and $67°$) became less intense, implying a transformation of Mg and Al_2O_3 support into magnesium-alumina compounds as well as an inactive spinel phase [23]. Therefore, we concluded that the high activity of $LiNO_3/Al_2O_3$ and $Ca(NO_3)_2/Al_2O_3$ is attributed to the major presence of active metal oxides formed by the sufficient thermal decomposition of nitrate precursors in air during the calcination step.

3.2. Effect of calcination temperatures

Since the calcination temperature largely affects the structural and catalytic properties of the resultant catalysts, we treated the impregnated catalyst samples at various temperatures to attempt to optimize this. As summarized in Table 4, $Mg(NO_3)_2/Al_2O_3$ calcined at all tested temperatures showed the lowest activity. The ME contents never exceeded 10%. This should be due to the major presence of an inactive magnesium-alumina phase in the catalyst as indicated in Fig. 1. On the other hand, the calcination at temperatures higher than 450 °C remarkably retarded the formation of ME over $Ca(NO_3)_2/Al_2O_3$. At the calcination temperature of 850 °C, $Ca(NO_3)_2/Al_2O_3$ gave the ME content of only 4%.

The XRD patterns of $Ca(NO_3)_2/Al_2O_3$ catalysts calcined at various temperatures indicated a decrease in the peaks corresponding to CaO simultaneously with the presence of calcium-aluminate compounds when the calcination was performed at higher temperatures (Fig. 2). Moreover, the peaks of calcium aluminate ($2\theta = 14.5°$, $29.4°$, $32.5°$, $37.9°$ and $45.6°$) were increased with the temperature. It was also found that the XRD patterns of the catalysts calcined at 650 and 850 °C were quite similar to that of $Mg(NO_3)_2/Al_2O_3$

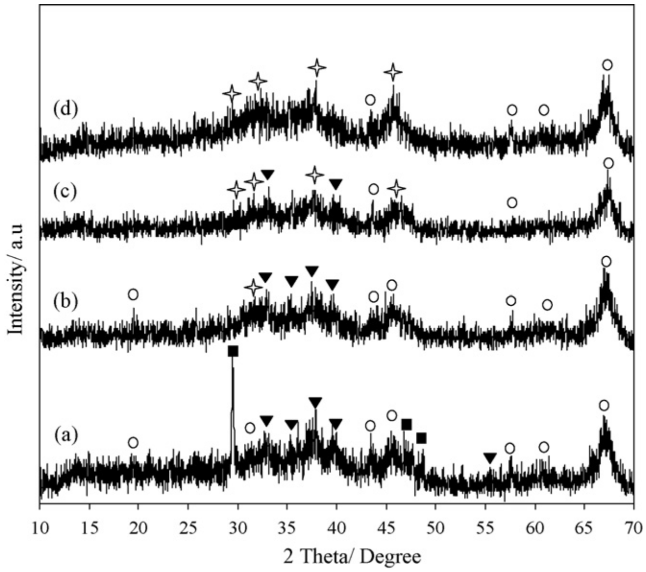

Fig. 2. XRD patterns of $Ca(NO_3)_2/Al_2O_3$ catalyst calcined at various temperatures: 450 °C (a), 550 °C (b), 650 °C (c), and 850 °C (d). (Symbols: (■) nitrate salts, (▼) metal oxides, (☆) metal-aluminate compounds, and (◯) Al_2O_3).

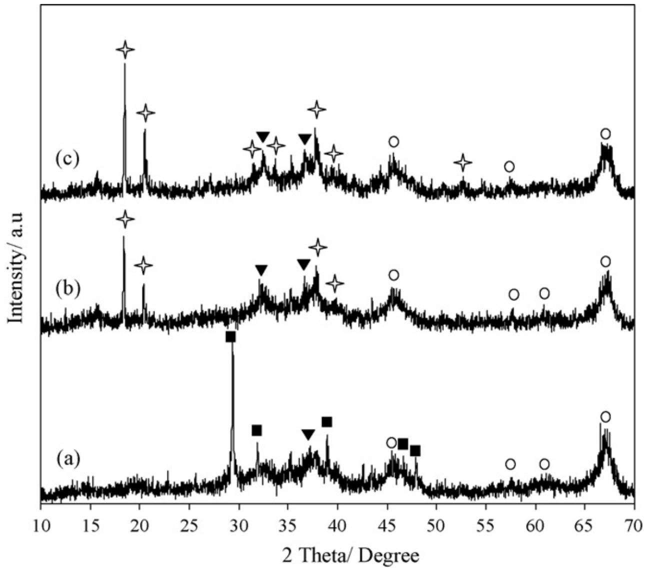

Fig. 4. XRD patterns of $NaNO_3/Al_2O_3$ catalyst calcined at various temperatures: 450 °C (a), 550 °C (b), and 850 °C (c). (Symbols: (■) nitrate salts, (▼) metal oxides, (☆) metal-aluminate compounds, and (◯) Al_2O_3).

(Fig. 1), suggesting the formation of a less basic and less active calcium-aluminate phase.

In contrast, the ME content was improved dramatically when using $LiNO_3/Al_2O_3$, $NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3 calcined at 550 °C as the catalysts (Table 4). The ME contents >90% could be achieved. With further increasing the temperature, the ME content obtained over $NaNO_3/Al_2O_3$ remained high, but $LiNO_3/Al_2O_3$ and KNO_3/Al_2O_3 exhibited a gradual drop of ME contents. At the temperature of 850 °C, while the formation of ME over $LiNO_3/Al_2O_3$ catalyst was mostly retarded, only $NaNO_3/Al_2O_3$ still gave the high ME content, 94.7%. Under the same calcination conditions, the ME content was decreased to 54.4% when KNO_3/Al_2O_3 was used as the catalyst.

Compared to the observed XRD pattern at 450 °C, there was no significant change when $LiNO_3/Al_2O_3$ catalyst was calcined at 550 °C (Fig. 3). In contrast, the formation of Na_2O (Fig. 4) and K_2O (Fig. 5) was enhanced, together with the presence of a small amount of corresponding alkali-aluminate compounds, after performing the calcination at 550 °C. These alkali metal oxides are generally considered as the catalytically active sites for the heterogeneously base catalyzed transesterification reactions [21]. However, the investigation of elemental composition of $NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3 calcined at 550 °C before and after being used in the transesterification indicated that ca. 70 and 45 wt.% of Na_2O and K_2O, respectively, were leached during the reaction, whereas $Ca(NO_3)_2/Al_2O_3$ catalyst exhibited a loss of CaO only ca. 8 wt.% (Table 5). The dissolution of active Na_2O and K_2O can

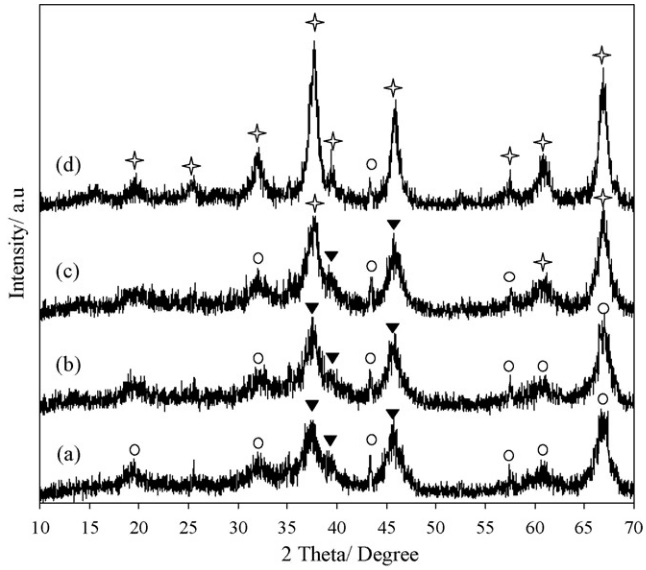

Fig. 3. XRD patterns of $LiNO_3/Al_2O_3$ catalyst calcined at various temperatures: 450 °C (a), 550 °C (b), 650 °C (c), and 850 °C (d). (Symbols: (■) nitrate salts, (▼) metal oxides, (☆) metal-aluminate compounds, and (◯) Al_2O_3).

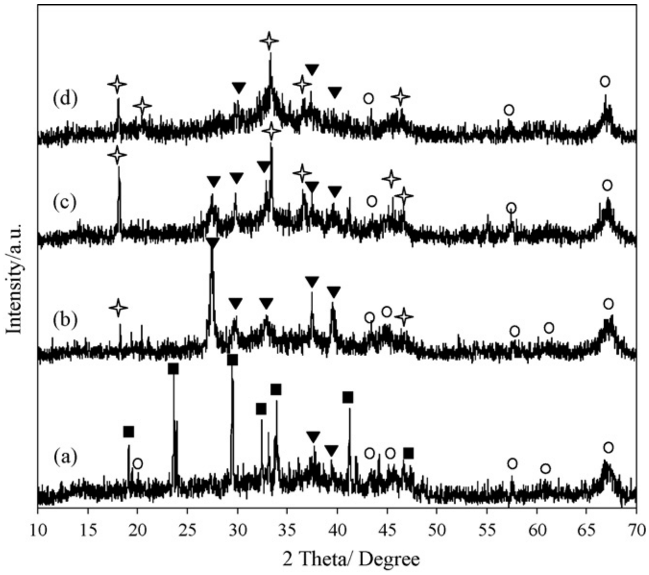

Fig. 5. XRD patterns of KNO_3/Al_2O_3 catalyst calcined at various temperatures: 450 °C (a), 550 °C (b), 650 °C (c), and 850 °C (d). (Symbols: (■) nitrate salts, (▼) metal oxides, (☆) metal-aluminate compounds, and (◯) Al_2O_3).

Table 5
XRF elemental analyses of catalysts calcined at 550 °C before and after being used in transesterification reaction

Component	Elemental composition (%)					
	$NaNO_3/Al_2O_3$		KNO_3/Al_2O_3		$Ca(NO_3)_2/Al_2O_3$	
	Before	After	Before	After	Before	After
Al_2O_3	85.09	94.89	44.26	68.23	44.94	49.83
Na_2O	13.74	4.10	0	0	0.16	0.15
K_2O	0.37	0.14	55.65	31.59	0.25	0
CaO	0.13	0.12	0	0	54.33	49.63
Others	0.67	0.75	0.09	0.18	0.32	0.39

occur via following reactions:

$$Na_2O + CH_3OH \rightarrow CH_3O^-Na^+ + OH^-Na^+ \quad (1)$$

$$K_2O + CH_3OH \rightarrow CH_3O^-K^+ + OH^-K^+ \quad (2)$$

This result suggests that, when $NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3 as well as $LiNO_3/Al_2O_3$ were used as the catalyst, the reaction mainly proceeds through the conventional homogeneous catalysis, yielding the high ME content. This is consistent with the recent demonstration of the leaching effect on the transesterification activity and catalytic behavior of an Al_2O_3-supported potassium catalyst [17].

At the higher calcination temperatures of 650 and 850 °C, the peaks related to a lithium-aluminate compound on $LiNO_3/Al_2O_3$ catalyst appeared (Fig. 3c and d). With increasing the temperature, the intensity of these peaks (2θ = 19.5°, 32°, 37.7°, 45.9°, 60.8° and 67°) was increased at the expense of Li_2O phase. This result indicates an increase in the formation of lithium-aluminate phase with the temperature. As discussed on the results obtained from $Ca(NO_3)_2/Al_2O_3$ and $Mg(NO_3)_2/Al_2O_3$, this phase is less active, rendering the ME content decreased.

The formation of alkali-aluminate compounds was also observed from XRD patterns of $NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3 catalysts, as shown in Figs. 4 and 5, respectively, when performing the calcination at high temperatures. The presence of sodium aluminate was indicated by the peaks at 2θ = 18.4°, 20.3°, 32.5°, 33.6°, 35.1°, 37.8° and 50.7° (Fig. 4b and c). On the other hand, the peaks at 2θ = 18.1°, 20.5°, 33.3°, 36.6°, 45.9° and 46.6° suggested the formation of potassium aluminate on KNO_3/Al_2O_3 catalyst (Fig. 5c and d). In contrast to other catalysts, although the alkali-aluminate compounds were formed, the ME content was not reduced so severely (Table 4). This should be attributed to the fact that $NaAlO_2$ and $KAlO_2$ can dissolve in water to give a very strong basic solution, while other alkali aluminates are less or non-soluble oxides [24]. Indeed, using commercial $NaAlO_2$ as the catalyst revealed the ME content as high as 92% under the same reaction conditions. Thus, the high ME contents from $NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3 catalysts calcined at high temperatures are likely to have also occurred via the homogeneous catalysis.

From the above results, we conclude that $Ca(NO_3)_2/Al_2O_3$ calcined at 450 °C is the most suitable catalyst for the heterogeneously catalyzed transesterification of PKO with methanol. Although the supported alkali metal oxides formed at high enough calcination temperatures are catalytically active for the transesterification (Table 4), the catalysis proceeds principally by the homogeneous pathway. Too high calcination temperatures resulted in the formation of less active oxides, probably the alkali- or alkali earth-aluminate phases. The except ion here is for $NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3 that formed soluble strongly basic $NaAlO_2$ and $KAlO_2$, respectively. Hereafter, $Ca(NO_3)_2/Al_2O_3$ catalyst calcined at 450 °C is applied to study the influences of reaction conditions in the transesterification of PKO and CCO.

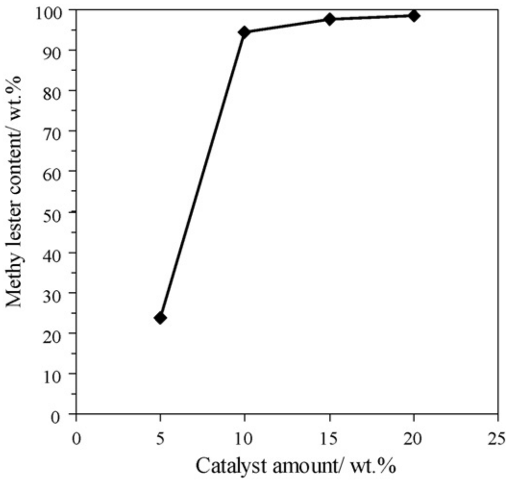

Fig. 6. Dependence of methyl ester content on catalyst amount in the transesterification of PKO over $Ca(NO_3)_2/Al_2O_3$. Reaction conditions: methanol/PKO molar ratio, 65; temperature, 60 °C; time, 3 h.

3.3. Effects of reaction conditions

The effects of catalyst amount and methanol/oil ratio on the ME formation in the PKO transesterification are showed in Figs. 6 and 7, respectively. Dependence of the ME content on the amount of catalyst indicated that, when using PKO as the starting oil, applying $Ca(NO_3)_2/Al_2O_3$ catalyst calcined at 450 °C for 10 wt.% yielded the ME content of 94% (Fig. 6). However, reducing a half amount of the catalyst to 5 wt.% decreased the ME content remarkably, while increasing more catalyst amount to 15 wt.% did not enhance the formation of ME significantly. Therefore, a 10 wt.% of $Ca(NO_3)_2/Al_2O_3$ is the suitable catalyst amount for the transesterification of PKO.

As illustrated in Fig. 7, with increasing the methanol/oil ratio from 33 to 65, the ME content was increased. At the ratio of 65, the highest ME content of 94 was attained. There was no significant improvement in the ME formation with a further increase in the ratio to 80. Our previous study [25] showed that when the methanol/oil ratio was decreased to 33, the ME content could be maintained as high as 90% by the addition of tetrahydrofuran (THF) as a co-solvent. However, the use of THF in a biodiesel production

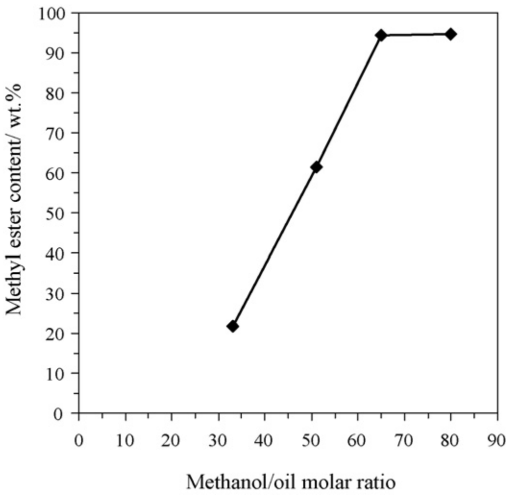

Fig. 7. Dependence of methyl ester content on methanol/PKO molar ratio over $Ca(NO_3)_2/Al_2O_3$ catalyst. Reaction conditions: catalyst amount, 10 wt.% based on amount of PKO; temperature, 60 °C; time, 3 h.

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

Properties	Standard of diesel fuel	Standard of biodiesel	Biodiesel from PKO	Biodiesel from CCO
Kinematic viscosity (cSt)	1.8–4.1	3.5–5	2.8	2.8
Specific gravity at 15.6/15.6 °C	0.81–0.87	0.86–0.90	0.87	0.87
Cetane index	>47	>51	56.5	53.2
Flash point (°C)	>52	>120	125	120
Heating value (MJ/kg)	–	–	36.5	41.9

process brings about additional handling precautions with both safety and economic and environmental costs. In the present study, the appropriate molar ratio of methanol/oil for the transesterification of PKO over $Ca(NO_3)_2/Al_2O_3$ catalyst is 65.

Compared to the previous reports [13–16], it can be seen that our transesterification system uses a relatively large amount of methanol. This increased methanol requirement could be explained by the observation above that the calcined $Ca(NO_3)_2/Al_2O_3$ exhibited a real heterogeneous catalysis in which the mass transfer between the immiscible liquid phases and the solid catalyst surface is a major limitation. The larger amount of methanol would then facilitate the diffusion of reactants and the formation of active methoxide species, resulting in a higher ME content. In contrast, other supported alkali catalysts exhibited the loss of active surface oxides simultaneously with the liberation of metal and hydroxide ions into the reaction mixture. Consequently, the transesterification occurs to a significant extent via a homogenous catalysis in which the mass transfer limitation is less restricted. Thus, even at the low methanol/oil ratios [13–16], the high ME contents can be achieved.

Fig. 8 shows dependence of the ME content on the catalyst amount in the transesterification of CCO. Compared to the PKO transesterification at the same catalyst amount (10 wt.%), the ME content of 85% was obtained when using CCO as the starting oil. This is about 8% lower than the case of PKO. Relatively large amount of $Ca(NO_3)_2/Al_2O_3$ catalyst, ca. 15 wt.%, was required to produce the biodiesel with the comparable ME content (94%). It could be ascribed to the higher free fatty acid (acid value) in CCO (Table 2), which results in a deactivation of some basic sites of the catalyst through the acid–base neutralization [20]. Using the catalyst amount of 20 wt.% can improve the ME content to 99.8%. Therefore, the suitable amount of $Ca(NO_3)_2/Al_2O_3$ catalyst in the transesterification of CCO is in the range of 15–20 wt.%.

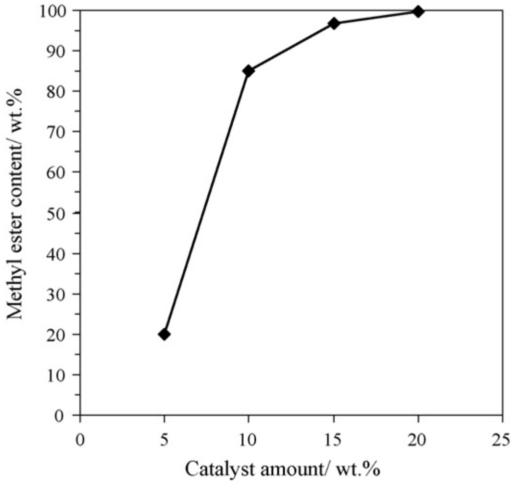

Fig. 8. Dependence of methyl ester content on catalyst amount in the transesterification of CCO over $Ca(NO_3)_2/Al_2O_3$. Reaction conditions: methanol/CCO molar ratio, 65; temperature, 60 °C; time, 3 h.

3.4. Biodiesel quality

Table 6 shows the physical and fuel properties of the biodiesel produced from PKO and CCO via the transesterification with methanol over $Ca(NO_3)_2/Al_2O_3$ catalyst, determined according to ASTM methods. Compared to the standard of diesel fuel and biodiesel issued by the Department of Energy Business, Ministry of Energy, Thailand, the specific gravity, cetane index and flash point of biodiesel from both vegetable oils met the requirement but their kinematic viscosity was significantly lower. This is likely to be attributed to the fatty acid composition of both oils which mainly consist of C_{12} (Table 1), rendering the resulting biodiesel less viscous. However, the viscosity of both biodiesel can be categorized in the standard of diesel fuel. Therefore, they could be applied to a diesel engine as an additive or a main component of diesel fuel.

4. Conclusions

The heterogeneously catalyzed transesterification of PKO and CCO was studied using various Al_2O_3-supported alkali and alkali earth metal oxides, prepared through the conventional impregnation method, as the catalysts to produce the biodiesel with a high ME content under batch conditions at 60 °C. The calcination temperature was found to largely influence the catalytic activity of the resultant catalysts, except for $Mg(NO_3)_2/Al_2O_3$ that exhibited very low ME content at all temperatures. $Ca(NO_3)_2/Al_2O_3$ and $LiNO_3/Al_2O_3$ yielded the high ME contents (>90%) when the calcination was performed at 450 °C. With increasing the temperature, the ME contents were dropped due to the formation of inactive metal aluminates. On the contrary, the activity of $NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3 catalysts was remarkably improved when the calcination was carried out at >550 °C. However, the XRF elemental analysis suggested the dissolution of the basic oxides from the supported alkali catalysts during the reaction. Therefore, in the present study, $Ca(NO_3)_2/Al_2O_3$ calcined at 450 °C was found to be the most suitable heterogeneous catalyst.

The suitable conditions for the transesterification of PKO and CCO with methanol over $Ca(NO_3)_2/Al_2O_3$ catalyst are the methanol/oil ratio = 65, temperature = 60 °C, reaction time = 3 h, and the appropriate catalyst amount = 10 wt.% and 15–20 wt.% for PKO and CCO, respectively. Importantly, the key physical and fuel properties of biodiesel from the heterogeneously catalyzed transesterification of both CCO and PKO meet the standards of diesel fuel and biodiesel issued by the Department of Energy Business, Ministry of Energy, Thailand.

Acknowledgements

The authors would like to thank Chumporn Palm Oil Industry Co. Ltd. for the palm kernel oil sample, and the Department of Materials Science, Faculty of Science, Chulalongkorn University for the XRD analyses. This work was supported by Petroleum and Petrochemical Technology Consortium and Graduate School, Chulalongkorn University.

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