

# Methanolysis of soybean oil over KCl/CaO solid base catalyst for biodiesel production

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**ABSTRACT:** A KCl-doped CaO catalyst synthesized by a wet impregnation method under microwave irradiation was studied in the transesterification of refined soybean oil with methanol at 338 K. The catalyst was characterized using powder X-ray diffraction, N<sub>2</sub> adsorption-desorption, transmission electron microscopy, and FT-IR techniques. The basic strength of the catalysts was also determined by the Hammett indicator method. The KCl/CaO catalyst exhibited a chemical stability in the reaction medium as well as a good resistance to feedstocks with high acidity.

**KEYWORDS:** transesterification

## INTRODUCTION

The limited supply of fossil fuels and current environmental concerns stimulates the production of alternative fuel from renewable resources worldwide. Biodiesels constitute a suitable alternative fuel as they are renewable, less toxic, and biodegradable<sup>1</sup>. The transesterification of vegetable oils is commonly performed using a catalytic processes resulting in the desired products at a reasonable rate<sup>2</sup>. Homogeneous-catalysed transesterifications of vegetable oils and animal fats cause major drawbacks such as instrument corrosiveness, difficulty in catalyst separation, and health hazards to the operators due to the generation of massive waste stream from washing steps<sup>3</sup>. In contrast, the transesterification reaction in the presence of heterogeneous catalyst generate products easier to separate and to purify, making the production process more economical and causing less environmentally damage<sup>4,5</sup>.

Calcium compounds, although of lower basic strength than Sr and Ba, are less toxic, widely available, cheaper, ease to handle, making them promising catalyst and/or catalyst support in the biodiesel industry<sup>6,7</sup>. The catalytic activity of CaO can be accelerated with an initial pretreatment with methanol at room temperature<sup>8</sup> activation at high temperature<sup>4</sup>, and/or surface modification to the catalyst support with potassium halides to generate strong active basic sites<sup>9–11</sup>. The last approach is of current interest to improve the catalytic activity of the supported catalyst<sup>9–11</sup>. In contrast to the conventional heating

techniques, the use of microwave irradiation on chemical syntheses offers several advantages – cleaner and faster reactions by introducing remotely the energy consumed, instantaneous energy input on-off system, lower thermal inertia, delivery of energy through the mass of the products not at surface, and scaling-up of the reaction. For this reason, microwave-heating technique is expected to be more efficient for the synthesis, enhancing the safety conditions and eliminating the waste generation<sup>12</sup>.

In this work, KCl-doped CaO catalyst was synthesized by a wet impregnation method under microwave irradiation. The activity of the prepared catalyst was evaluated in transesterification of refined soybean oil with methanol. To investigate the new phase developed after impregnation and activation, powder X-ray Diffraction (PXRD), FT-IR techniques were also performed.

## MATERIALS AND METHODS

Commercial refined soybean oil (RSBO) with an acid value of 0.4 mg KOH/g was purchased from a local store. CaO was obtained as lime from a natural resource in Thailand. Oleic acid (C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>, 90% purity, Aldrich), methanol (CH<sub>3</sub>OH, ACS grade, Aldrich), and potassium chloride (KCl, Ajax) were used as received. A microwave oven was M181 GN Samsung household microwave with an operating power output from 100–850 W, 7 power levels, and 35 min dual-speed timer.

### Preparation of catalysts

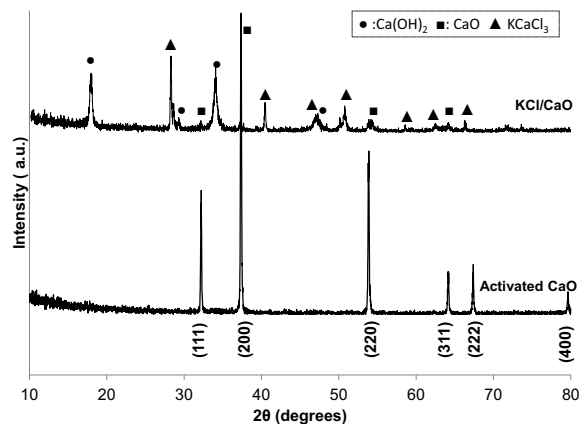
KCl/CaO catalyst was prepared using a wet impregnation method under microwave irradiation with some modifications of a reported method<sup>13</sup>. Typically, 2 g of lime was slowly immersed into 15 ml of aqueous KCl solution (0.45 mol of KCl/mol of support, lime) with stirring and left the mixture for 2 h at room temperature under continuous stirring. Thereafter, the white mixture was heated up to 353 K for additional 2 h, and then irradiating the resulting slurry in a microwave oven operating to a power of 100 W for 10 min. Finally, the solid was calcined at 773 K for 3 h in air and the material was collected as KCl/CaO.

### Characterization of catalysts

PXRD, N<sub>2</sub> adsorption-desorption, transmission electron microscopy (TEM), FT-IR techniques, and the Hammett indicator method were used to characterize the catalysts. PXRD patterns were acquired on a Bruker D8 ADVANCE diffractometer using Cu-K<sub>α</sub> radiation ( $\lambda = 0.15406$  nm) operating at 40 kV and 40 mA over a wide angle ( $2\theta$  range of 10–80°) with a step size of 0.015° at a scanning speed of 0.6° min<sup>-1</sup>. The Brunauer, Emmet, and Teller (BET) specific surface area and pore volume of the catalysts were measured by nitrogen adsorption-desorption isotherm at -196 °C in a Quantachrome Autosorb-1 model surface area and pore size analyser. Sample degassing was performed at 120 °C for 24 h under vacuum before measurement. The TEM image of KCl/CaO catalyst was recorded on a transmission electron microscope (FEI Tecnai G<sup>2</sup> 20/30) operating with an accelerating voltage of 120 kV. FT-IR spectra were recorded on a Perkin-Elmer system 2000 spectrometer in the 4000–1000 cm<sup>-1</sup> scanning range with a resolution 4 cm<sup>-1</sup> (KBr pellet technique). Samples were dried at 393 K overnight prior to measurement. The basic strengths of the catalysts were determined by the Hammett indicator method, expressing an acidity function ( $H_-$ )<sup>14</sup>. The used indicators were bromothymol blue ( $pK_{BH} = 7.2$ ), phenolphthalein ( $pK_{BH} = 9.3$ ), Nile blue ( $pK_{BH} = 10.1$ ), and 2,4-dinitroaniline ( $pK_{BH} = 15.0$ ). About 200 mg of the catalyst was dispersed in a 10 ml of 0.02 M methanol solution of the indicator and the mixture obtained was left for 2 h for equilibration.

### Catalytic performance in transesterification of soybean oil

The laboratory scale transesterification was conducted in a 100 ml two-necked flask equipped with a water-cooled reflux condenser in an oil bath with a magnetic



**Fig. 1** PXRD patterns of calcined CaO and KCl/CaO catalysts.

stirrer. In a typical experiment, the reaction mixture of refined soybean oil (10 g) to methanol (5.49 g, 7.03 ml) and 3 wt% of freshly prepared catalyst referred to refined soybean oil was used with a fixed stirring rate of 500 rpm at 338 K for 1 h in air. The reaction was started after introducing the desired amount of methanol (methanol to RSBO 15:1 mol/mol) and 3 wt% catalyst into the flask containing preheated refined soybean oil up to 338 K. After reaction, a small quantity of aliquot was sampled and cooled down in an ice-bath to stop the reaction and the sample was then mixed with n-hexane/water system to extract the ester product. The n-hexane phase was dried with anhydrous sodium sulphate and was sequentially removed by purging with nitrogen. The sample was analysed in a 300 MHz <sup>1</sup>H NMR spectrometer (Bruker DPX 300). The biodiesel yield was determined by the integration ratio of the signals of methoxy group (3.67 ppm; s, -OCH<sub>3</sub>) of the fatty acid methyl ester to the signal of the  $\alpha$ -carbon methylene group (2.3 ppm; t, - $\alpha$ -CH<sub>2</sub>) for all fatty acid derivatives<sup>15</sup>.

## RESULTS AND DISCUSSION

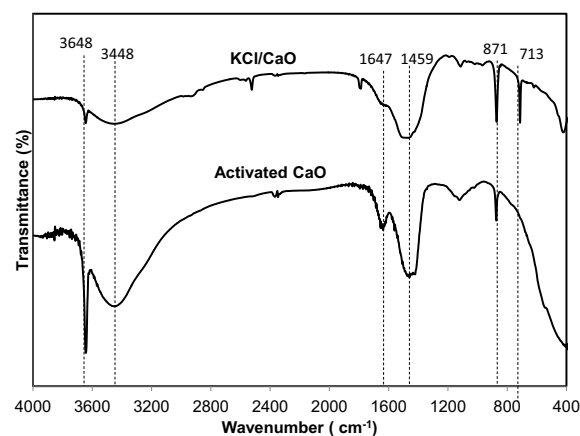
### Catalyst preparation and characterizations

From the PXRD patterns in Fig. 1, the CaO solid activated at 1073 K for 5 h displayed well-resolved CaO peaks indexed as (111), (200), (220), (311), (222), and (400) diffractions. After calcination at 773 K for 3 h, KCaCl<sub>3</sub> and Ca(OH)<sub>2</sub> phases were generated, associated with minor CaO peaks in KCl/CaO catalyst. It would be suggested that the new active phase, KCaCl<sub>3</sub> was generated from the proper impregnation of the dopant solution into the support lattice by capillary action and later activation process.

**Table 1** Basic strengths and catalytic performances of solid base catalysts by initial screening test (methanol to oil (15:1) molar ratio, 3 wt% catalyst based on RSBO weight, 338 K, 1 h).

Catalyst	$T_c$ (K)	Basic strength ( $H_-$ )	KCl to CaO (molar ratio)	K (mmol/g)	Ca (mmol/g)	Biodiesel (%)	TON ( $\times 10^{-2}$ ) (on K)	TON ( $\times 10^{-2}$ ) (on Ca)
Activated CaO	1073	$9.7 < H_- < 15.0$	-	-	17.86	79.5	-	169.7
KCl/CaO	773	$9.7 < H_- < 15.0$	0.45	5.03	11.16	93.5	708.4	319.3

$T_c$ : calcination temperature, TON: turnover number.

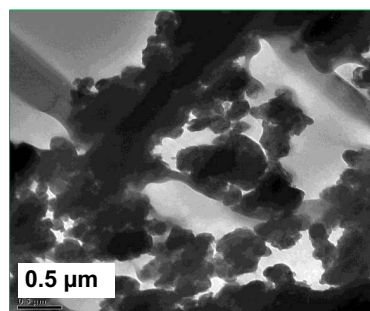


**Fig. 2** FT-IR spectra of the activated CaO and KCl/CaO catalysts.

The basic strengths and catalytic performances of the solid bases determined by the Hammett indicator method are summarized in Table 1. It was observed that calcined CaO and KCl/CaO solids exhibited the basic strengths in the range of 9.8–15.0. The basic strength of KCl/CaO is similar to that of CaO, probably indicating the effect of  $\text{Ca}(\text{OH})_2$  phases on the catalyst surface.

From the FT-IR spectra as depicted in Fig. 2, sharp stretching bands at  $3648 \text{ cm}^{-1}$  were assigned to the structural OH groups of  $\text{Ca}(\text{OH})_2$  as reported<sup>4</sup>. The broad band at  $3448 \text{ cm}^{-1}$  and a small weak peak at  $1647 \text{ cm}^{-1}$  were assigned to the stretching and bending bands of adsorbed water on the catalyst surface<sup>13</sup>. The broad band at  $1459 \text{ cm}^{-1}$  and absorption bands at 713, 877 were attributed to asymmetric stretch, out-of plane bend and in plane bend vibration modes, respectively, for  $\text{CO}_3^{2-}$  ions for solid catalysts<sup>16</sup>. There were no  $\text{K}_2\text{O}$  phases observed on the catalyst surface.

Based on the TEM image as shown in Fig. 3, the KCl/CaO catalyst possesses porous structure with large grains. The nitrogen adsorption-desorption isotherm data revealed that the KCl/CaO catalyst

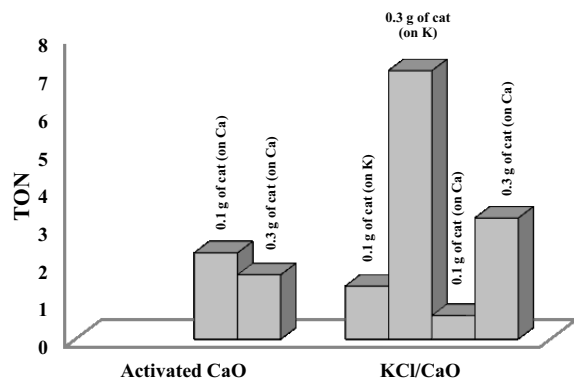


**Fig. 3** TEM image of KCl/CaO catalyst.

had a porous structure with specific surface area of  $8.4 \text{ m}^2/\text{g}$  and the average pore size of 36.1 nm which was comparable to the CaO catalyst with specific surface area of  $10.3 \text{ m}^2/\text{g}$  and the average pore size of 46.3 nm. Thus it can be concluded that the better contact between substrate and methanol on the porous catalyst surface could enhance the efficiency of this catalytic reaction.

#### Catalytic performance of KCl/CaO catalyst in transesterification reaction

As shown in Fig. 4, KCl/CaO catalyst showed a dramatic increase in biodiesel yield up to 93.5% using 3 wt% catalyst loading corresponding to 6.1% yield of biodiesel on 1 wt% catalyst. It can be suggested that the available active sites are enough to react with free fatty acid and triglyceride, leading to the completion of reaction<sup>11</sup>. On the other hand, increasing KCl/CaO catalyst loading could increase the turnover numbers (TONs) for the reaction on both potassium and calcium amount. In contrast, higher loading of activated CaO catalyst decreased the TON values, meaning that external mass transfer limitation of the CaO solid. Potassium halide doped-CaO catalyst could increase higher TONs over the same amount of catalyst loading (3 wt%) compared to that of activated CaO (see Table 1). The higher catalytic activity of KCl/CaO catalyst over CaO is probably due to the contribution of the new active species ( $\text{KCaCl}_3$ ) which

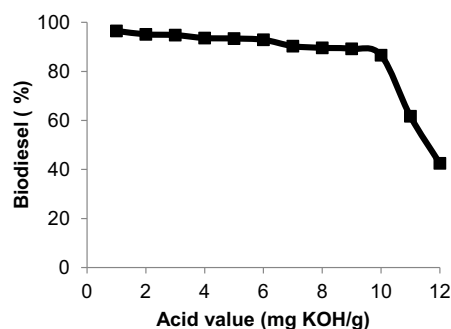


**Fig. 4** The turnover numbers for transesterification reactions over different loadings of activated CaO and KCl/CaO catalysts. Reaction conditions: methanol/oil (15:1) molar ratio, 338 K, 1 h.

is probably a strong Lewis acid with strong attraction for  $\text{CH}_3\text{O}^-$  but weaker than  $\text{KCaF}_3$ <sup>10</sup>. The catalytic activity depends on its concentration and the tendency to form methoxide ion. Therefore,  $\text{Cl}^-$  may act as a weak base for the proton abstraction from methanol to facilitate the conversion of methanol to methoxide ion in the KCl/CaO system much more than the CaO system. Furthermore, the nucleophilic attack of the resulting more populated methoxide ions to the carbonyl group of triglyceride enhanced the activity of KCl/CaO catalyst rather than the CaO system.

#### Resistance of KCl/CaO catalyst to raw material with high acidity

The influence of a substrate with high acid value on the biodiesel yield is also an important parameter for base-catalysed transesterification. In general, base-catalysed transesterification is limited to feedstocks with high FFA levels that are neutralized with base catalysts to form soap (saponification). Soap poisoning at the active site resulted in catalyst deactivation reducing biodiesel yield<sup>17</sup>. As shown in Fig. 5, the anti-poisoning ability of KCl/CaO catalyst was carried out with oils of different acid values in the range of 1–12 mg KOH/g prepared by mixing variable amounts of oleic acid with refined soybean oil. The transesterification was then conducted with 15:1 mol/mol of methanol to oil and 3 wt% catalyst at 338 K for 2 h. Interestingly, the KCl/CaO catalyst displayed a resistance to high acidity up to acid values of 10 mg KOH/g of oil giving biodiesel yield in the range of 87–97%. It probably appears to come from the contribution of new developed potassium calcium chloride,  $\text{KCaCl}_3$  crystalline structure. On the other



**Fig. 5** Acid resistance of KCl/CaO catalyst. Reaction conditions: methanol to oil (15:1) molar ratio, 3 wt% of catalyst loading, 338 K, 1 h.

hand, the new  $\text{KCaCl}_3$  phase could uniformly disperse on the surface of the catalyst support after calcination to possess the KCl/CaO catalyst in good stability with high acid resistance.

#### Evaluation of leaching in the reaction system and reusability of the catalyst

In heterogeneous catalysis, the stability of catalyst is as important as its activity for the suitability as a specific solid catalyst for biodiesel production more economical. In order to know the solubility of such catalyst in the reaction system, the extent of active site leaching of KCl/CaO catalysts was carried out over 3 wt% of catalyst mixed with 7.03 ml of methanol, without soybean oil and stirred for 1 h under 338 K. The catalyst was removed by immediate filtration with suction pump and then the filtrate was added to the preheated soybean oil<sup>10</sup> and the reaction run for 1 h at 338 K. Then it showed that no biodiesel was produced indicating the good chemical stability of the catalyst in the reaction medium. In order to evaluate the catalyst durability, the catalyst recycling experiments were also carried out under the same reaction parameters. After each cycle, the catalyst was recovered by centrifugation and used for next run. The experimental results demonstrated that the catalyst could be reused 7 cycles, giving 82–93% yield of biodiesel.

#### CONCLUSIONS

In summary, KCl-doped CaO catalyst was successfully synthesized under microwave irradiation. The KCl/CaO catalyst demonstrated a good resistance to high acid values of oil until 10 mg KOH/g, achieving 87–97% yield of biodiesel. The transesterification reaction was also heterogeneously catalysed by KCl/CaO solid.

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