



Short communication

Gel-combusted Ca-based catalysts for methanolysis of palm oil



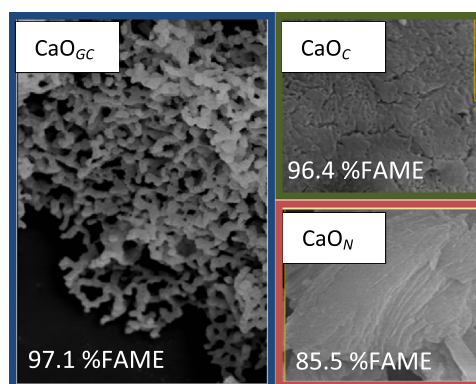
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HIGHLIGHTS

- Submicron-sized CaO catalysts from gel-combustion synthesis.
- Significant improvement of basic sites as compared with conventional ones.
- Effective biodiesel production via methanolysis of palm oil.
- FAME content >96.5% within 90 min and at mild reaction temperature of 60 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

Gel-combustion technique was applied to synthesize CaO catalysts for effective biodiesel production via palm oil methanolysis. The developed catalyst was a group of submicron-sized bonded CaO particles with meso-to-macro interparticle porous structure. Thus, this structure provided much smaller particle size, higher specific surface area and porosity, compared to the CaO from direct calcination of Ca nitrate or carbonate. Among the catalysts studied, the gel-combusted CaO exhibited the highest amounts of basic site, providing the highest catalytic activity in the methanolysis. The FAME content of >96.5% (Thailand national standard) was obtained over gel-combusted CaO within 90 min and at mild reaction temperature of 60 °C.

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1. Introduction

Biodiesel is one of the major diesel substitutes, presently used as a diesel blend in the Asean Economic Community (AEC) countries. Biodiesel is obtained from catalytic transesterification of vegetable oils or animal fats with small chain alcohols [1]. The

heterogeneous catalyst has been developed because it overcomes the disadvantages of the homogeneous catalysts (e.g. NaOH and KOH) [2]. With the heterogeneous catalysis approach, the catalyst removal unit by water washing could be eliminated, hence the processing time and the capital and operating costs would be minimized. Among various solid catalysts, calcium oxide (CaO) is considered the most promising catalyst for methanolysis at nearly comparable reaction conditions to the conventional process [3–5]. Calcium oxide has many advantages over other catalysts, such as, good activity, good reusability, and inexpensive material.

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Commonly, calcium oxide catalysts are synthesized from various calcium precursors by direct calcination method [6,7]. The calcination usually takes place above the phase transformation temperature of $\text{Ca}(\text{OH})_2$ and CaCO_3 . Therefore, an external heat source is necessary in this method. The resultant CaO catalyst typically provides micron-sized dense particles with low surface area of $1\text{--}2\text{ m}^2\text{ g}^{-1}$ [8,9]. Therefore, the development of CaO catalysts with improved physicochemical properties including surface area, pore volume and basicity to carry out the methanolysis of oil proficiently under mild conditions remains an intriguing challenge. In recent years, several researches were devoted to catalyst synthesis by using gel-combustion method [10,11]. This synthesis technique would produce very fine crystalline oxide powders.

The present paper investigated the gel-combustion synthesis of calcium-based catalyst for methanolysis of palm oil. The calcium oxide catalysts from simple calcinations of Ca nitrate and carbonate precursors were also studied for comparison. The physicochemical properties of the development catalyst were thoroughly investigated. The correlation between the observed property and the methanolysis activity was then studied and discussed.

2. Experimental

2.1. Chemicals and catalyst preparation

For direct calcination method, $\text{Ca}(\text{NO}_3)_2$ (99%, Ajax Finechem) and CaCO_3 (99%, Ajax Finechem) precursors were, respectively, calcined at 600 and 800 °C for 4 h. The resultant samples were labeled as CaO_N and CaO_C , respectively. In the gel-combustion synthesis, $\text{Ca}(\text{NO}_3)_2$ was used as a Ca precursor, and citric acid (99.0%, Ajax Finechem) was used as fuel and gelling agent. The stoichiometric composition is calculated based on the total oxidizing and reducing valences of the oxidizer and fuel. First an aqueous solution of $\text{Ca}(\text{NO}_3)_2$ and citric acid was stirred at 120 °C until a gel of thickened liquid formed. The Ca-complex gel was further heated at 420 °C until fine oxide powders were obtained. Before being used as a catalyst in the methanolysis, the powder was calcined at 800 °C for 4 h to completely form calcium oxide phase. The catalysts were labeled as CaO_{GC} . To avoid the catalyst deactivation by air atmosphere, all catalysts were immediately used after the catalyst activation in a furnace.

2.2. Characterization of the catalyst

The nitrogen sorption system (BELSORP-Max, BEL., Japan) was employed to determine specific areas and pore volumes of the catalysts. X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advanced X-ray diffractometer, operated at 40 kV, 40 mA, and a 2θ range of 30–70° with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406\text{ nm}$). The particle morphology was characterized by scanning electron microscope (JSM 6301F, JEOL, Japan). Temperature-programmed desorption using CO_2 as a sorption gas (CO_2 -TPD) was used to study basic property of the catalysts. The CO_2 -TPD was carried out using a Quantachrome ChemBET Pulsar Automatic Chemisorption Analyzer. Before CO_2 adsorption, a sample (0.3 g) was outgassed and purged with helium with at 300 °C for 30 min. The sample was exposed to a flow of pure CO_2 at 25 °C for 2 h, and then the system was flushed with helium for 30 min. The CO_2 -TPD was carried out under a helium flow at a flow rate of 30 ml min^{-1} , while the temperature was ramped from room temperature to 900 °C with a ramping rate of $10\text{ }^\circ\text{C min}^{-1}$, and held at the final temperature for 30 min. The CO_2 desorption was monitored by a thermal conductivity detector (TCD).

2.3. Reaction procedures

The methanolysis reactions were carried out in a 250 ml three-necked flask equipped with a condenser. Methanol (Carlo Erba Reagenti) and catalyst were mixed under magnetic stirring rate of 600 rpm. The reaction temperature was constantly controlled at 60 °C. A methanol to palm oil (refined palm olein grade) molar ratio of 18:1 was used with 10% catalyst to oil ($w_{\text{catalyst}}/w_{\text{oil}}$) in all experiment. The method used for the analysis of FAME content (wt%) was the European Standard EN 14103. The FAME content was analyzed by a gas chromatography (GC-2010, Shimadzu). Reusability of the catalyst was also investigated. After the reaction test was completed, the spent catalyst was recovered by centrifugal and used for the next run without any treatment.

3. Results and discussion

3.1. Catalyst characterization

The morphology of the CaO catalysts was depicted in the SEM micrographs of Fig. 1. CaO_{GC} showed the coral-like structure which contained submicron-sized particles bonded together as a porous network (Fig. 1(a)). The pore size between branched particles was in a range of micron scale. The surface area would be mainly contributed by interparticle external surface. This kind of morphology could be attributed to the liberation of a large amount of gases during combustion reaction. The formation of large amount of gases during combustion inhibited solid particle size growth, and favored formation of submicron to nano-sized powders with high specific surface area [11]. The combusted sample comprised two major morphologies: (1) cubic crystals with obvious edges (Fig. 1(b)) and (2) irregular faceted steps (Fig. 1(c)). Both CaO_N and CaO_C were considered to be less-porous, and the particle size should directly respond to the surface area.

As shown in Table 1, CaO_N and CaO_C had extremely low specific surface area of 0.2 and $1.2\text{ m}^2\text{ g}^{-1}$, and low total pore volumes of 0.080 and $1.161\text{ cm}^3\text{ g}^{-1}$, respectively. CaO_{GC} provided a significant improvement of surface area and total pore volume of $10.4\text{ m}^2\text{ g}^{-1}$ and $10.261\text{ cm}^3\text{ g}^{-1}$, respectively. CaO_N and CaO_C showed extremely low sorption capacity of N_2 , suggesting their non-porous characteristics. The N_2 sorption isotherm of CaO_{GC} was classified into Type II (non-porous or macroporous) or Type IV (mesoporous). The sorption capacity of CaO_{GC} was significantly improved, but not as high as one found in common porous materials. Nonetheless, the small hysteresis loop suggested a minor portion of mesopores in the sample (see Supplementary materials Fig. S1). According to XRD analysis, all samples were formed in a crystalline phase of CaO (see Supplementary materials Fig. S2). CO_2 -TPD results suggested the presence of basic sites over the catalysts (see Supplementary materials Fig. S3). All samples provided basic sites with difference in desorption characteristics. CaO_{GC} showed a basic amount of $1547\text{ }\mu\text{mol g}^{-1}$. CaO_N and CaO_C revealed similar desorption behaviors; they possessed two major functions of first region at 450–650 °C and second region at 650–800 °C. CaO_N had the lowest basic site of $168\text{ }\mu\text{mol g}^{-1}$, while CaO_C possessed basic amount of $732\text{ }\mu\text{mol g}^{-1}$. There was a minor peak at 230–270 °C that could represent the basic site of surface OH^- group from $\text{Ca}(\text{OH})_2$. The basicity of OH^- species was relatively low compared to that of O_2^- [12]. It was reported that CaO calcined from calcium carbonate showed the CO_2 desorption peak at 542 and 605 °C, respectively, while CaO calcined from calcium nitrate was less active and could not be measured the amount of CO_2 adsorbed [13]. The reported data were consistent with the present results that CaO_N gave less amount of basic sites than CaO_C . It is clear that the gel-combusted sample was well-crystallized and possessed higher surface area,

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