



Preparation and application of binary acid–base CaO–La₂O₃ catalyst for biodiesel production



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ABSTRACT

A simple method was developed for biodiesel production from non-edible Jatropha oil which contains high free fatty acid using a bifunctional acid–base catalyst. The acid–base catalyst comprising CaO and La₂O₃ mixed metal oxides with various Ca/La atomic ratios were synthesized via co-precipitation method. The effects of Ca/La compositions on the surface area, acidity–basicity and transesterification activity were investigated. Integrated metal–metal oxide between Ca and La enhanced the catalytic activity due to well dispersion of CaO on composite surface and thus, increased the surface acidic and basic sites as compared to that of bulk CaO and La₂O₃ metal oxide. Furthermore, the transesterification reactions resulted that the catalytic activity of CaO–La₂O₃ series were increased with Ca/La atomic ratio to 8.0, but the stability of binary system decreased by highly saturated of CaO on the catalyst surface at Ca/La atomic ratio of 10.0. The highest biodiesel yield (98.76%) was achieved under transesterification condition of 160 °C, 3 h, 25 methanol/oil molar ratio and 3 wt.%. In addition, the stability of CaO–La₂O₃ binary system was studied. In this study, Ca–La binary system is stable even after four cycles with negligible leaching of Ca²⁺ ion in the reaction medium.

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1. Introduction

Recently, the worldwide biodiesel production has grown sharply. Biodiesel (fatty acid methyl esters, FAMES) is a renewable, biodegradable, non-toxicity and alternatives (or extender) for transportation fuel (conventional petroleum based diesel fuel). The physicochemical and fuel properties of biodiesel are grouped into the same range as petroleum diesel. Thus, it can be applied to compression-ignition diesel engines with little or no modification [1,2].

Generally, biodiesel can be derived from natural and renewable domestic source of triglycerides (vegetable oil). With the concern of edible oil rivalry between food and fuel purpose, unpractical usage of over-expensive materials in actual production of biodiesel contributed to the shift of biodiesel feedstock from edible resources to non-edible resources [3–6]. *Jatropha Curcas* oil, a potential inedible source of biodiesel, has drawn the interesting of both government and private sectors for biodiesel production, lately.

The current technologies for biodiesel production are based on homogeneously catalyzed transesterification under basic conditions (NaOH or KOH). Non-edible jatropha oil consists of high free fatty acids (FFAs) content, is cheaper in prices as compared to edible oil due to its inferior nutritional value, low market demand and high availability. The conventional basic catalysts (NaOH and KOH) are sensitive to high content of FFAs, which led to formation of soap and complicates the product separation as well as reduces the biodiesel content. Numerous studies have been carried out by using two step acid–base catalyzed reactions. The first acid catalyzed treatment is used to reduce FFA to <1 wt.% via esterification followed by base catalyzed transesterification of treated oil to high grade biodiesel. However, the main concerns are the high material cost (excess methanol), post-treatment cost (multi-purification and water washing) to remove homogeneous catalyst, additional treatment to neutralize the pH for first and second processes. Furthermore, the content of treated oil and final biodiesel product were reduced during separation and washing step. Thus, the high acid *J. curcas* oil is not feasible to be employed in conventional approach for biodiesel production in view of its incompatibility to the homogeneous catalysts [7,8].

To optimally exploit the high FFA content *J. curcas* oil in biodiesel production, a new easy-to-operate heterogeneous catalytic system

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which is capable of performing mild esterification and transesterification with minimal soap formation is highly desirable. Such integrated solid catalyst furnish with bifunctional acid–base system where the Lewis acid sites involve to esterification reaction of carboxylic acid with methanol and the conjugated basic sites activate the transesterification of triglyceride with methanol in one-pot reaction. In contrast with two steps homogeneous acid and base catalyze reactions, heterogeneous catalyst equipped with acid–base properties may render many inherent advantages.

Previous research indicated that CaO, either from natural waste shell or limestone or chemical Ca salt are widely used as an active base catalyst for transesterification studies [9–14]. Conjugation between CaO and metal oxides with different basicity/acidity is able to enhance the basicity or provides acid–base active sites for transesterification process. Currently, some of the heterogeneous mixed metal oxides are reported to be active in transesterification reaction because they are tolerance to high FFAs and water in vegetable oil. Previously, we have successfully established that the improvement of basicity and catalyst's stability by integrated CaO with MgO or ZnO. The mixed metal oxide (CaO–MgO and CaO–ZnO) by ameliorate the basicity were highly active in transesterification of low grade jatropha oil. Furthermore, strong stability of these binary metal oxide system provide higher quality biodiesel yield with less leaching of active metal ion, better reusability and highly tolerance to FFA as compare to pure CaO [15–17]. Recently, a bifunctional acid–base mixed metal oxide catalyst, ZnO–La₂O₃ which capable of catalyzing esterification and transesterification reaction simultaneously in a single step for unrefined or waste oil with high water and FFAs content. The strong interaction between Zn and La species was induced by the presence of both basic and acid active sites which found to simultaneously catalyze the fatty acid esterification and oil transesterification reactions while minimizing oil and biodiesel hydrolysis. Approximately of 96% of biodiesel content was yielded at the high reaction temperature (220 °C) after 3 h of reaction even with crude palm oil, crude soybean oil, waste cooking oil, food-grade soybean oil with 3% water and 5% oleic acid addition [18].

In this study, binary metal oxides comprised of CaO and La₂O₃ with adequate acid–base properties were synthesized via co-precipitation method. The potential materials use for catalyst synthesis are Ca and La, it is anticipated that Ca–O consist of basicity that suitable for triglyceride transesterification whereby La²⁺ render the acidic properties that preferable for esterification of free fatty acid. The physicochemical properties and catalytic activity of its bulk oxides and mixed metal oxides were studied. The prepared binary oxide catalyst has been used in biodiesel production via transesterification of non-edible jatropha oil with methanol, to assess the technology's ability in order to meet quality specification for biodiesel. Furthermore, the recyclability of the catalysts has been investigated to determine its binary system stability.

2. Experimental

2.1. Catalyst preparation

Catalysts with different Ca/La atomic ratios (0.5–10.0 atomic%) were prepared using co-precipitation method. In a typical catalyst preparation procedure, the required amount of Ca(NO₃)₂·4H₂O and La(NO₃)₃·6H₂O was dissolved in deionized water. The two precursor solutions were mixed homogeneously and allowed to precipitate using a NaOH and Na₂CO₃ basic solutions at a constant pH of 10 and controlled by slow addition in metal salt mixture. The sample was stirred for 24 h at 60 °C. Finally, the precipitate formed was then filtered, washed until the pH of the filtrate was 7 and dried at

100 °C overnight. The sample was calcined at 950 °C for 6 h after drying based on the TGA analysis (Supplementary data). Thermal activated catalysts were denoted as CL0.5, CL2, CL4, CL6, CL8 and CL10 with incremental Ca/La atomic ratios of 0.5, 2.0, 4.0, 6.0, 8.0 and 10.0 atomic%, respectively.

For comparison, the bulk CaO was prepared using the same procedure as above (co-precipitation method). The precursor for the oxide was formed after the dropwise addition of precipitant agent of Na₂CO₃ and NaOH solution into the aqueous solution of Ca(NO₃)₂·4H₂O at room temperature. The mixture was then under vigorous stirring for 24 h at 60 °C. The white solid was centrifuged and washed with deionized water and dried at 100 °C. The CaO obtained after calcinations in air for 800 °C for 6 h based on several literature reviews [11,19].

2.2. Catalysts characterization

The powder X-ray diffraction (XRD) analysis was carried out with a Shimadzu diffractometer model XRD6000. The diffractometer employed Cu-K_α radiation to generate diffraction patterns from powder crystalline samples at ambient temperature. The Cu-K_α radiation was generated by a Philips glass diffraction X-ray tube (broad focus 2.7 kW type).

The total surface area of the catalysts was obtained using a Brunauer–Emmer–Teller (BET) method with nitrogen adsorption at –196 °C. Analysis was conducted using a Thermo Finnigan Sorptomatic 1900 series nitrogen adsorption/desorption analyzer.

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) was used to obtain information about the morphology and size of the samples. The morphology study of the catalysts was carried out using a JEOL scanning electron microscope model JSM-6400 while elemental chemical analysis done with the EDS technique. Furthermore, bulk metal content present in the catalysts was determined by using Inductive coupled plasma-Atomic emission spectrometer (ICP-AES), PerkinElmer Emission Spectrometer Model Plasma 1000.

The basicity and the basic strength distribution of the catalysts were studied by temperature-programmed desorption using CO₂ as probe molecule. TPD-CO₂ experiment was performed using a Thermo Finnigan TPDRO 1100 apparatus equipped with a thermal conductivity detector. Catalysts (0.1 g) were pretreated under a helium stream at 800 °C for 30 min (10 °C min⁻¹, 30 mL min⁻¹). Then, the temperature was decreased to 50 °C, and a flow of pure CO₂ (30 mL min⁻¹) was subsequently introduced into the reactor for 1 h. The sample was flushed with helium at 50 °C for 30 min before the CO₂ desorption analysis. The analysis of CO₂ desorption was then carried out between 100 and 1000 °C under helium flow (10 °C min⁻¹, 30 mL min⁻¹) and detected by thermal conductivity detector (TCD). The acidity of the catalyst was determined by using ammonia (NH₃) as a probe gas. The adsorption and desorption of NH₃ was followed the same steps as TPD-CO₂ method. The amount of basicity/acidity of the catalyst were determined by the shape of the CO₂/NH₃ desorption peak from the data of area under the graph that provided. The temperature of the peak maximum (*T*_{max}) at which the desorption of CO₂/NH₃ occurred used to study the characteristic and basic/acid site distribution of the active sites for the catalysts.

The chemical stability of the binary metal oxide catalyst was investigated by analyzing the presence of free metal content in the biodiesel product which could be attributed to the occurrence of leaching. The biodiesel product from the reusability test was analyzed without further purification step by atomic absorption spectrometer (AAS-S Series; Thermo Scientific, San Jose, CA). The concentration of Ca content (ppm) in biodiesel produced was detected.

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