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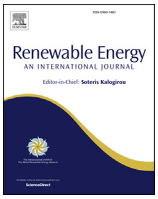

Synthesis, characterization and catalytic activity studies of lanthanum oxide from Thai monazite ore for biodiesel production

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ABSTRACT

Rare earths in Thai monazite ore were separated by chemical process following purification by an ion exchange process technique. They were utilized as raw materials to synthesize solid catalysts for the production of biodiesel. The novel solid catalysts were prepared by the simple oxalic acid precipitation method. The prepared CeO_2, La_2O_3 and Nd_2O_3 catalysts were employed to catalyze transesterification of palm oil and methanol. They showed high catalytic activity with FAME content over 95%. The catalytic performance of the best available La_2O_3 catalyst was additionally investigated. It was found that the initial transesterification rate catalyzed by the synthesized La_2O_3 catalyst was three times higher than its commercial counterpart, which related to its basic strength, high crystallinity, large pore volume and great crystallite size. The highest FAME content of 95% was achieved within 45 min under the optimal conditions of 200 °C reaction temperature, 39 bar reaction pressure, 1:30 molar ratio of oil to methanol, 10 wt% catalyst loading and 600 rpm stirring rate. In addition, the novel La_2O_3 catalyst was observed to be stable even after four recycle runs with insignificant loss of catalytic activity.

1. Introduction

Recently, world energy demand has started increasing rapidly because of increases in population and industrialization. The current reserves of fossil fuel such as coal and natural gas are finite and will be totally consumed shortly [1]. In addition, the use of these fuels contributes to global warming. Therefore, research related to renewable biofuels is being developed and strongly promoted. Biodiesel is perceived as a promising alternative fuel to replace conventional diesel fuel [2]. Biodiesel can be derived from renewable biological sources such as vegetable oils, waste cooking oils, grease and animal fats. It shows several advantages: it is biodegradable and non-toxic, and has lower emissions than fossil fuel in terms of the release of carbon monoxide, sulfur oxides, unburned hydrocarbons and particulate matters. It is also safer for handling and storage, with a relatively high average flash point value of 150 °C [3–5].

Normally, biodiesel is produced via transesterification of vegetable oils and methanol in the presence of a catalyst. The conventional homogeneous base catalysts (e.g., KOH, NaOH, CH_3OK and CH_3ONa) exhibit much higher catalytic efficiency under mild reaction conditions (temperature of 60 °C, atmospheric pressure and reaction time of 1 h) [1,6]. However, these catalysts have several drawbacks and limitations: high sensitivity to FFA and water content in feedstock oils leading to soap formation, difficulties in recovering the catalyst, substantial wastewater generation and intensive energy use [7,8]. An additional drawback of homogeneous base catalysts is that they cannot be regenerated and reused [6]. Homogeneous acid catalysts (e.g., H_2SO_4, HCl and $R{-}SO_3H$) favor both esterification and transesterification simultaneously for biodiesel production of oils with high content of FFA. Nevertheless, the homogeneous acid catalyst reaction requires a higher amount of alcohol, higher reaction temperature and pressure, and a longer reaction time to reach complete conversion compared to the homogeneous base catalyst reaction. Other disadvantages with this catalyst are corrosion and environmental problems [6,9].

Several heterogeneous catalysts have been developed to overcome the disadvantages of homogeneous catalysts. A simple metal oxide like CaO has been reported as an active base catalyst in

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transesterification of vegetable oils to biodiesel in various literature [4,10,11]. However, the active surface sites of CaO could be easily poisoned by contact with H_2O and CO_2 in air, resulting in the loss of catalytic activity. In addition, the leaching of CaO active species into the reaction medium led to the formation of calcium soap and deactivation of the catalyst activity [3,12,13]. MgO has weak basicity and poor solubility in methanol. It has been used as a catalyst in transesterification of soybean oil. However, a high reaction temperature (523 °C) and high pressure (24 MPa) are needed to obtain a high biodiesel yield [14]. In the case of heterogeneous acid catalysts, their activity performance is still lower compared to alkali/base catalysts. They require high reaction temperatures and have relatively slow reaction rates [12]. Therefore, it is of great important to develop novel heterogeneous catalysts having high catalytic activity, selectivity and stability for biodiesel synthesis.

Rare earth oxides (REOs) – for example, La_2O_3, Nd_2O_3 and CeO_2 – have been used as catalysts and as promoters or additives in catalysts to improve thermal stability and catalytic performance in transesterification reactions [1,3,4,15–22]. La_2O_3 has been extensively investigated as one of the most promising among the REO catalysts for biodiesel production because it possesses both acid and basic site properties, which favor simultaneous transesterification and esterification [23]. Russbueldt and Hoelderich [15] have investigated the preparation of the La_2O_3 catalyst by the precipitation method. The La_2O_3 catalyst showed high catalytic activity for transesterification of rapeseed oil. The highest FAME yield of 97.5% was obtained with 50% methanol at 200 °C. The strong basicity of the solid catalyst led to this excellent activity. Zhou et al. [16] have studied two kinds of nano La_2O_3 catalysts prepared using sonochemical and hydrothermal methods. These catalysts were used in the transesterification of refined *J. curcas* L. oil (JCO) with methanol for biodiesel production. The nano La_2O_3 catalysts from the sonochemical preparation method showed promise with a FAME yield of 97%, significantly higher compared to conventional La_2O_3. The relatively high activity of the catalysts might be due to their high base strength, large base amount, small particle size and large BET surface areas.

The Thailand Institute of Nuclear Technology has undertaken research on the separation and purification of rare earth elements from Thai monazite ore. The monazite ore was obtained from tin mining in the south of Thailand and was found to be composed of rare earth elements such as CeO_2 (30.37%), La_2O_3 (10.84%), Nd_2O_3 (10.67%), Y_2O_3 (2.78%), Pr_6O_{11} (2.13%), Gd_2O_3 (1.11%) and Dy_2O_3 (0.50%). The alkali decomposition method at temperature of 140 °C for 3 h was used to break down the monazite ore. The mixed rare earth hydroxide cake was then fed to ion exchange process for the separation and purification as indicated in the previous studies [24–26]. The relatively high purities of Ce, La and Nd up to 92% or more, were obtained at a good yield.

In this study, the purified Ce, La and Nd obtained from the above decomposition process were used as raw materials for the synthesis of CeO_2, La_2O_3 and Nd_2O_3 catalysts. The catalysts were prepared via a simple oxalic acid precipitation method and used for biodiesel production. The best available La_2O_3 catalyst was selected to study its catalytic activity in the transesterification of palm oil. The effect of reaction parameters, including the reaction temperature, molar ratio of oil to methanol, and catalyst loading on the initial reaction rate and biodiesel content, were investigated. The physicochemical properties of the prepared catalyst were also determined. In addition, catalyst reusability and regeneration were evaluated.

2. Materials and methods

2.1. Synthesis of rare earth oxide catalysts

Each EDTA solution of Ce, La and Nd, which was obtained from the decomposition process of Thai monazite ore, was separated and purified. Each was then precipitated using 10 wt% of oxalic acid at the flow rate of 1 ml/min under constant stirring (400 rpm) until pH reached to 3–4. The suspension stood at room temperature overnight. The white precipitate of the rare earth oxalate was filtrated and then washed with distilled water several times. The cake was dried at 110 °C for 12 h and calcined at 900 °C for 3 h to obtained rare earth oxide (CeO_2, La_2O_3, Nd_2O_3) catalysts.

2.2. Catalyst characterization

The chemical composition of rare earth oxide catalysts was determined with the use of a PANalytical Epsilon 5 energy dispersive X–ray fluorescence (EDXRF) spectrometer. The catalyst sample was mixed with boric acid (99.5%, Sigma Aldrich, Germany) binding material in a sample: acid ratio of 4:1. The mixture was thoroughly ground and pressed to a pellet using a 15 ton hydraulic press for 45 s before EDXRF analysis.

The powder X–ray diffraction (XRD) pattern of the catalysts was recorded on a PANalytical X'Pert PRO X–Ray diffractometer equipped with Cu Kα radiation ($\lambda = 1.5406$ Å) operating at 45 kV and 40 mA and a step size of 0.02°. The measurement was performed in the 2θ range of 20–90°.

The N_2 adsorption–desorption measurement was performed on an Autosorb–1 automatic surface analyzer (Quantachrome Instruments). The surface area was analyzed according to the Brunauer–Emmett–Teller (BET) method using adsorption data over the relative pressure range of 0.05–0.30. The total pore volume was calculated based on nitrogen volume at the highest relative pressure. The average pore diameter was determined by the Barrett–Joyner–Halenda (BJH) method using desorption data of the isotherms. Prior to measurements, each catalyst was degassed at 300 °C for 18 h under vacuum.

The TGA analysis was performed on a Mettler Toledo, TGA/SDTA 851e in the range of 25–1100 °C and the heating ramp of 20 °C/min.

The surface morphology of the sample was observed by scanning electron microscopy, SEM (S–3400N, Hitachi).

A Perkin Elmer Spectrum One (FTIR) spectrometer was used to record FTIR spectra with 4 cm^{-1} resolution by KBr pressed disc technique. The scanning range was from 400 to 4000 cm^{-1}.

The acid and base strength of the catalysts was determined using Hammett indicators. Approximately 25 mg of catalyst sample was shaken with 1 ml of ethanol solution, Hammett indicator (0.1 wt%) and left to equilibrate for about 2 h or no color changes. The indicators used for the measurements of acid and base strength were methyl red ($pK_a = 4.8$), neutral red ($pK_a = 6.8$), bromothymol blue ($pK_a = 7.2$), phenolphthalein ($pK_a = 9.3$) and nile blue ($pK_a = 10.1$). The expression of acid and base strength was in terms of Hammett acidity function (H_0) and Hammett basicity function ($H\_$), respectively.

The surface acidity and basicity of the catalyst was determined by the titration method. For acidity, a suspension of catalyst (0.05 g) in 0.02 M of NaOH (5 ml) was stirred at a rate of 400 rpm. After stirring the suspension for 1 h, the mixture was titrated with 0.02 M of HCl using 0.01% of phenolphthalein in ethanol as the indicator. In the case of basicity determination, the catalyst was mixed with 0.02 M of HCl, and the amount of HCl adsorbed to the catalyst was determined by titration with NaOH.

The basic site properties of the catalyst were measured by temperature programmed desorption of CO_2 (TPD) using a