Evaluating the optimum operating parameters of biodiesel production process from soybean oil using the Li_2TiO_3 catalyst

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ABSTRACT

This study focuses on the transesterification of soybean oil into biodiesel using Li_2TiO_3. Li_2TiO_3 is prepared through a solid-state reaction that involves mixing and grinding TiO_2 and Li_2CO_3 followed by the calcination at 800 °C for 2 h. The prepared Li_2TiO_3 is characterized by X-ray diffraction (XRD), Field Emission Scanning Electron Microscope (FE-SEM), and BET, and the Hammett indicator is applied to obtain their physical and chemical properties. Li_2TiO_3 has never been studied as a solid catalyst for transesterification reaction. Under optimal reaction conditions, namely a methanol:oil molar ratio of 24:1, a catalyst amount of 6 wt%, and a reaction temperature of 65 °C for 2 h, a biodiesel conversion rate of 98.5% is obtained. Moreover, different vegetable oil and used cooking oil are used as the raw materials for the biodiesel production. Li_2TiO_3 can be easily recovered and reused for ten cycles without significant deactivation.

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1. Introduction

The increasing pollution and the shortage of fuels have forced human beings to search for sustainable use of the remaining resources. Biodiesel has been alternatively used for preventing human and environment from the problems of consuming non-renewable energy sources as fossil fuels [1–3].

Heterogeneous solid catalysts have several advantages, such as easy separation of catalysts, recyclability, and eco-friendliness [4–7]. Hence, the purification and washing steps can be eliminated from the process. Furthermore, it is interesting to modify the structures of surface metal oxide species in order to improve their catalytic properties for specific applications. Among all alkali metals (Li, Na, K) with these modification properties, alkali metals contain the strong base sites, either as bulk or supported metal oxide (SiO_2, Al_2O_3) [8,9], and the structure and the catalytic properties of the surface alkali metals species are strongly influenced by the metal oxide supports. However, this reaction is associated with several difficulties in using basic solid catalysts, from an industrial perspective, involving the surface active sites being easily decayed upon exposing the catalyst to air. Most of the basic solid catalysts need to be resolved the removal of water and carbon dioxide from the surfaces to enhance their catalytic activities [10]. In earlier studies [11–13], found that lithium silicate and Li_2CO_3 catalyt-

ically tolerated the exposure to air. Therefore, lithium silicate and Li_2CO_3 had great potential for the use as a catalyst. Additionally, Li-based catalysts show a very high activity promoting transesterification reaction [14,15]. Dai et al. [14] reported that the $LiAlO_2$ catalyst was prepared by solid-state reaction and enhanced the conversion. Chen et al. [15] reported that the significant enhancement of catalytic activity was achieved for Li_2CO_3 with SiO_2, leading to a highest basicity. Modification of previously synthesized catalysts with SiO_2 and Al_2O_3 to improve the structure and catalytic properties was strongly influenced by the factors [16,17].

TiO_2 is well known to be a cheap, readily available and nontoxic oxide support in catalytic reactions. TiO_2 is used in various catalytic applications due to the unique combination of properties, such as stability, relatively high surface area, sintering resistance, resistance to poisoning, and low cost which make it an attractive potential catalyst for many reactions [18]. It is obvious that the use of TiO_2 can make the synthesized catalyst products much more cost-effective. TiO_2 has the potential for commercializing a prepared catalyst because of its low cost, high yield, and easy control.

In this paper, the Li_2TiO_3 catalyst is prepared and applied to biodiesel production through the transesterification of soybean oil. To the best of our knowledge, this is the first attempt to use Li_2TiO_3 as a catalyst for biodiesel production. The process parameters with the most significance in affecting biodiesel production from catalyzed transesterification of soybean oil include calcination temperature, calcination time, methanol/oil molar ratio, catalyst amount and reusability. Moreover, the catalyst reuse in various

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oil transesterification reactions is evaluated in order to perform a biodiesel production.

2. Materials and methods

2.1. Catalyst preparation

Soybean oil (TTET Union Co., Taiwan), methanol (ACS grade, ECHO Chemical Co., Taiwan), TiO_2 (Shimakyu's Pure Chemicals, Osaka, Japan), CaO (Shimakyu's Pure Chemicals, Osaka, Japan) and Li_2CO_3 (Shimakyu's Pure Chemicals, Osaka, Japan) were used as received. The fatty acid composition in the soybean oil as follows:11.2%, palmitic acid; 4.44%, stearic acid; 25.85%, oleic acid; 50.79%, linoleic acid; 6.06%, linolenic acid; and traces of other fatty acids.

The solid-state reaction was used for the preparation of Li_2TiO_3 oxide nanocomposite. TiO_2 powder was added to an aqueous solution containing Li_2CO_3. Finally, the mixture was thoroughly and the as-prepared solution was dried at 110 °C for 12 h, followed by calcinations in air at 700, 800, 900 and 1000 °C for 2 h.

2.2. Reaction procedures

The conversion of soybean oil to biodiesel was performed in a 250-ml flat-bottomed flask, equipped with a reflux condenser and a magnetic stirrer. The reactor was initially filled with 12.5 g of soybean oil, which was heated to 65 °C for 2 h while stirring at 300 rpm. The reactant was stirred evenly to avoid splashing in the flask at the stirring speed. The timing of the reaction was initiated as soon as the mixture of methanol and the catalyst was added into the reactor. The effects of molar ratio of methanol to oil (12:1–30:1), and catalyst/oil weight ratio (2–10 wt.%), on the conversion of triglycerides to biodiesel were investigated. All of the experiments were performed at atmospheric pressure. After the transesterification reaction, DI water was added into the reaction mixture to stop the reaction. The biodiesel and glycerol layers were easily separated due to differing densities, of 0.86 and 1.126 g/cm^3, respectively. A supernatant was filtered through a common filter paper, and then excess methanol and water were evaporated prior to FAME analysis.

2.3. Catalyst characterization

The base strength of the samples (H_) was determined using Hammett indicators [19]. Approximately 50 mg of the sample was shaken with 1 ml methanol solution of the Hammett indicator. 2 h were allowed to elapse for the reaching of equilibrium after which no additional change of color took place. The basic strength was defined as being stronger than the weakest indicator which exhibited a color change, and weaker than the strongest indicator which produced no color change. Bromthymol blue (H_ = 7.2), phenolphthalein (H_ = 9.8), 2,4-dinitroaniline (H_ = 15.0), and 4-nitroaniline (H_ = 18.4), at a concentration of 0.02 mol/l were obtained from Sigma–Aldrich (St. Louis, MO, USA) and used as Hammett indicators. The precipitates were further characterized. An X-ray powder diffractometer (XRD) (MAC Sience MXP18) was used to identify the crystalline species of catalysts. A Cu tube serving as the X-ray source was employed to estimate the active site phase, and the working voltage and current was 40 kV and 80 mA, respectively. The powdered samples were pressed onto suitable holders. The scanning range of 2θ was from 20° to 80°. Diffraction patterns were manually analyzed with the Joint Committee of Powder Diffraction Standard (JCPDS) card. Field emission scanning electron microscopy (FESEM; Model JSM-6700F, JEOL, Tokyo, Japan) operated at 5 kV accelerating voltage. FESEM was used to observe the morphologies of Li_2TiO_3. The samples were immobilized on the copper holder with the carbon glue. Before analysis, the holder with samples was pretreated at 200 °C. The Brunauer–Emmett–Teller (BET) surface area of the Li_2TiO_3 was measured at −196 °C by gravimetric methods with a BET-201-AEL apparatus. The BET surface area was calculated from the adsorption isotherm, and the ratio of pore volume and the average pore diameter was obtained from the pore size-volume distribution.

2.4. Analytical methods

The FAME concentration was calculated using the internal standard method (according to the EN 14,103 method). In this study, gas chromatograph (Thermo Trace GC Ultra, Thermo Co., Austin, Texas, USA.) equipped with a flame ionization detector and capillary column Tr-biodiesel (F), Thermo Co. (length 30 m, internal diameter 0.25 mm and film thickness 0.25 μm) using methyl heptadecanoate as an internal standard. Nitrogen was used as the carrier gas with a linear velocity of 2 ml/min. The oven temperature at 120 °C, held for 1 min, then the temperature program started at 120 °C with increase to 220 °C at a rate of 30 °C/min and an increase to 250 °C at a rate of 10 °C/min, reached 250 °C hold time of 2 min. The diluted solution with methyl heptadecanoate was added as an internal FAME standard. The most common peaks were observed at C16:0, C17:0, C18:0, C18:1, C18:2, and C18:3. The conversion was determined according to the following equation.

$$\text{Conversion}\% = \frac{\Sigma A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times A_{EI}}{m} \times 100\%$$

ΣA: sum of areas of all peaks ranging from C14:0 to C24:0, A_{EI}: heptadecanoic acid methyl ester IS area, C_{EI}: concentration (mg/ml) of heptadecanoic acid methyl ester solution, V_{EI}: volume of heptadecanoic acid methyl ester solution added to sample, m: mass of the sample (mg).

In order to quantitatively evaluate leaching of the solid base catalyst under the reaction conditions, some parts of the samples taken from the reactor were carefully filtered, and the residual methanol was evaporated in a rotary evaporator so that the FAME and glycerol were left as a separate phase. After the evaporation, the dry fraction was treated with 0.1 mol/l hydrochloric acid. The resulting solution was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectro Genesis) to determine the Li concentration.

3. Results and discussion

3.1. Reaction studies

Fig. 1 shows different calcination temperatures of Li_2TiO_3 through the transesterification process. With the calcination temperature at 700 °C, the conversion achieves 51.3%, and the higher conversion 98.5% appears on the calcination temperature at 800 °C. However, the transfer rate decreases at the calcination temperature 1000 °C. As can be seen, a calcination temperature of 700 °C is not sufficient to produce highly active Li_2TiO_3 for transesterification and, according to the XRD analysis, the deactivation of the catalyst after its calcination at high temperature is probably the result of the loss of active sites, by the sublimation and agglomeration into the structure. Therefore, the optimal calcination temperature is 800 °C in this study. Fig. 1 shows the transfer rate increases with calcination time and has a maximum value at 4 h at 800 °C. The result suggests that the main crystalline structure of the samples corresponding to TiO_2 is transformed to the Li_2TiO_3 phase after the solid-state synthesis with Li_2CO_3 is finished during 4 hrs at 800 °C.

The stoichiometric molar ratio of methanol to oil required for transesterification is 3:1 [20]. As shown in Fig. 2, the conversion