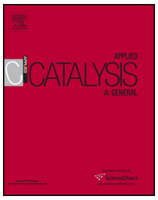
Applied Catalysis A: General 484 (2014) 122–133

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Transesterification of palm olein using sodium phosphate impregnated on an alumina support

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ARTICLE INFO

Article history:
Received 24 March 2014
Received in revised form 20 June 2014
Accepted 6 July 2014
Available online 11 July 2014

Keywords:
Transesterification
Heterogeneous catalyst
Sodium phosphate
Palm olein
Al_2O_3

ABSTRACT

In the present work, a new heterogeneous catalyst for fatty acid methyl ester (FAME) synthesis consisting of an active sodium phosphate (Na_3PO_4) component impregnated on an Al_2O_3 support was developed. Al_2O_3-supported Na_3PO_4 was prepared by incipient-wetness impregnation. The catalyst was characterized using XRD, FT-IR, SEM-EDX, and BET. The influences of reaction variables, such as the agitation intensity, the molar ratio of methanol/oil, the reaction temperature, and the catalyst amount, on the conversion of palm olein were investigated. The presence of free fatty acids and water are also studied in this research. The results showed that high FAME contents (>96%) can be achieved within 30 min at 210 °C with a methanol/oil molar ratio of 18:1 and 1.0 wt.% catalyst. The prepared Na_3PO_4/Al_2O_3 catalyst exhibited high stability and recyclability. In our tests, FAME production was slightly but not significantly reduced after 5 recycles. Elemental analysis by ICP-OES found a small amount of Na in the products following the reaction.

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1. Introduction

Biodiesel, which consists of fatty acid methyl esters (FAMEs), is produced by reacting vegetable oil and animal fats with alcohol has a similar properties to diesel derived from petroleum resources. The advantages of biodiesel are it biodegradable and can be used in existing engines without modification. Mixing biodiesel with diesel can improve the lubricity properties of diesel [1]. Various technologies have been studied to convert oil to biodiesel, and transesterification with a homogeneous base catalyst is currently the most used technique in industrial-scale production. This process allows for high conversions to be attained in a short time (<15 min) [2], but suitable to refined oil feedstocks that contain less than 0.5 wt.% water and 1 wt.% free fatty acids to avoid soap formation and attain high product yields [3,4]. Moreover, this process releases a large amount of waste water during the purification step.

Transesterification with heterogeneous catalyst is particularly attractive. The main advantage of a heterogeneous catalyst is its easy separation from the reaction product without a complex purification step, there by producing biodiesel that is more environmental friendly. Several compounds have been investigated as solid catalysts for biodiesel synthesis. The most commonly studied compounds are metal oxides and alkaline or alkaline–earth metal compound [5–7]. However, at present, the economical production of the ester and glycerol does not appear feasible. Currently, there is only one heterogeneous catalyst being used in industrially for biodiesel production. This catalyst consists of a mixed oxide of Zn and Al with a spinal structure [8,9].

The main disadvantage of solid catalysts operating at conventional reaction temperatures is the reaction rate is less than that of the homogeneous system due to the diffusion limitation of the three phases (oil/alcohol/catalyst). In addition, most of the solid catalysts currently used are in powdered form, which is mixed with the products, thus leading to difficultly in separation. Heterogeneous catalysts are continuously under development to solve these problems [10,11]. Normally, small metal particles are unstable at temperatures typical of catalytic reactions. One way to overcome this problem is to use structure promoters or catalyst supports, which can provide more specific area for active species to anchor. Various supports have been investigated to provide shape stability. Alumina oxide in the form of porous γ-Al_2O_3 has been widely used as a catalyst support because it offers a high surface area and high thermal stability [12,13].

However, the prepared catalysts on porous supports operated at reflux temperature suffer from a slow reaction rate because the

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http://dx.doi.org/10.1016/j.apcata.2014.07.007
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mass transfer resistance. Xie et al. [14] reported that 15 h of operation was required to obtain 65% conversion. Boz et al. [15] also reported that catalysts containing KI, KF, K_2CO_3, or KNO_3 on Al_2O_3 can require up to 8 h to obtain a 99% yield. Meso-structured supports have been shown to have improved catalytic performance compared to micro-structured supports, this improved performance could be due to reduced mass transfer resistance [16,17]. One way to increase the reaction rate is by increasing the reaction temperature. A CaO catalyst showed slow reaction rates at low temperatures, but when the reaction temperature was increased to 250 °C, complete conversion was obtained in 6 min [18,19]. Similarly, a $CaCO_3$ catalyst exhibited low conversion at low temperature, but complete conversion was obtained in 23 min at 200 °C [20]. Lukic et al. [21] studied reaction temperatures between 80 and 200 °C and concluded that increasing the reaction temperature resulted in a concomitant increase in product content. The catalytic ability of MgO [22] is quite weak at lower temperatures, but increasing the reaction temperature favorably influenced the methyl ester yield, resulting in high conversions within a few minutes. Transesterification at high temperatures can reduce the amount of catalyst required to achieve a particular degree of conversion within a specified time.

Besides, transesterification using a coupled catalyst requires milder reaction conditions but must also achieve product yields similar to other methods. Many researchers have reported the use of coupled catalysts under subcritical and supercritical conditions [23,24]. Jian et al. [25] studied the transesterification of soybean oil in supercritical methanol with sodium silicate. Wang et al. [26] found that adding NaOH to supercritical and subcritical conditions can increase conversion while reducing the critical state to a milder condition.

Generally, heterogeneous catalysts are in powdered form, which leads to separation difficulties following the reaction. In addition to powdered form, commercial catalysts are often available as pellets, pills, rings, spheres, granules or extrudates, and the use of these forms may facilitate downstream separation.

The previous work showed that Na_3PO_4 is a potential catalyst [27]. This catalyst is insoluble in both the product and reactant phases, but it is in powdered form and difficultly to separate from the reaction products. Hence, preparation of catalysts on large supports is investigated in this study because large supports are easy to separate from the reaction products and can be reused several times. Currently, while there have been several studies on large supports at the lab-scale, only one large catalyst support has been developed for industrial catalysis [8,9]. Therefore, the present work aims to develop a new catalyst for the transesterification of palm olein using Na_3PO_4 loaded on an alumina support. The catalyst was prepared using incipient-wetness impregnation of Na_3PO_4 on meso-pore alumina in ring form. XRD, BET, FT-IR, and SEM were used for characterization of the catalyst. The effect of reaction variables are agitation speeds, methanol/oil molar ratio, reaction temperature and catalyst amount. The effect of moisture and free fatty contaminate in feedstocks on the formation of methyl ester also studied in this work. ICP-OES was used for the elemental analysis of the prepared and spent catalysts and to analyze catalyst leaching. The fuel properties of the biodiesel produced using this process was also analyzed meet the biodiesel standards of Thailand.

2. Experimental

2.1. Materials

Commercial edible palm olein was purchased from a local food market, and industrial grade methanol (purity 99.84%) was used as a raw material in this research. Sodium phosphate dodecahydrate ($Na_3PO_4{\cdot}12H_2O$) was of analytical grade (Ajax Chemical). As a catalyst support, 1/4 in. ring-Al_2O_3 (Alfa Aesar) with a BET surface area of 166.63 $m^2\,g^{-1}$ was used.

2.2. Catalyst preparation

The Na_3PO_4 alumina-supported catalyst was prepared via incipient-wetness impregnation of aqueous solutions on an alumina support. Incipient-wetness impregnation utilizes a volume of water less than or equal to the amount required to fill the pores of the support material. Sodium phosphate was dissolved in deionized water at ambient temperature to a final concentration of 8.8 wt.%.

The support was first dried overnight in an oven and then subjected to vacuum to remove air and moisture from the catalyst pores. Sodium phosphate solution was then added slowly to the dried support. The impregnated catalyst was left overnight at room temperature and then dried at 105 °C for 24 h. The catalyst was then calcined at 500 °C for 5 h in air. The prepared catalyst was analyzed by ICP-OES, and loading of Na_3PO_4 on Al_2O_3 was calculated to be 6.5 wt.%.

2.3. Catalyst characterization

Electron probe microanalyzer (EPMA) images of the catalyst were obtained on a Shimadzu EPMA-1720 with optical image magnifications of 40× to 400,000×. An accelerating voltage of 20 kV was used for sample morphology determination and elemental analysis. Elemental analysis at various points on the sample was performed using a JEOL, JSM-7600F. Energy dispersive X-ray spectroscopy (EDX) was carrying out using a Jordan instrument.

The BET surface areas of the samples were measured using the multipoint N_2 adsorption-desorption method on a BEL BELSORP-max. All samples were degassed at 120 °C for 12 h under reduced pressure (<1 Torr) prior to the sorption measurements. The specific surface area (S_{BET}) of each sample was calculated using the Brunauer, Emmett, Teller (BET) method.

FT-IR spectra of the samples were measured using the KBr pellet technique. Spectra were recorded on a Perkin Elmer Spectrum One. The scanning range was from 300 to 4000 cm^{-1} under atmospheric conditions (5 mg of sample with 100 mg of KBr).

XRD measurements were performed on a Bruker AXS Model D8 Discover using Cu-Kα radiation over a 2θ range of 10–75° with a step size of 0.02°/step and a scanning speed of 0.5 s/step. The data were analyzed with DiffracPlus software, and phases were identified according to the power diffraction (PDF) database (JCPDS, International Centre for Diffraction Data).

Elemental analyses of the prepared catalyst, the spent catalyst, and the product samples were performed using Perkin Elmer Optima 3000 inductively coupled plasma. Each sample was digested before analysis by ICP-OES. The measured amounts of sodium and phosphate were compared to standards to determine actual concentrations.

2.4. Transesterification reaction procedure

The experiments were conducted in a 2-L stainless-steel autoclave equipped with a variable speed agitator (50–1500 rpm). The reactor could be heated while the temperature was controlled by a jacketed heating element. The reactor pressure was maintained at 800 psi with nitrogen gas. The catalyst was first put in a stainless steel basket that was placed in the middle of the reactor vessel. Palm olein was put into the reactor in predetermined amounts, and the feed bomb was filled with methanol. The system was then purged with nitrogen. Next, the reactor was heated to the desired temperature while the liquid was stirred at a constant speed. When the reactor reached the reaction temperature, methanol was fed

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