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Activity and basic properties of KOH/mordenite for transesterification of palm oil

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Abstract

The catalytic performance of KOH/mordenite has been studied for transesterification of palm oil using a batch reactor and a packed-bed reactor at 60 °C and atmospheric pressure. The KOH/mordenite processed transesterification in the batch reactor gave the highest methyl ester yield of 96.7% under optimum conditions, while a methyl ester content over 94.5% was obtained in the packed-bed reactor. This comparison indicates that transesterification in a batch-type reactor gives a higher methyl ester yield than that of a continuous-flow reactor. Dealumination was found in the calcined catalysts and had a significant effect on the physical structure and chemical composition of the catalysts. Leaching of the potassium species was negligible, whereas depositing and washing of the reacted mixture with acetone on the catalyst surface were observed by FTIR.

Key words

transesterification; biodiesel; mordenite; KOH; solid base catalyst

1. Introduction

Biodiesel fuels from transesterification of palm oil are being considered as a kind of potential biofuel to contribute toward sustainable development of many countries, including Thailand. The main advantages of using biodiesel as a fuel are its renewability, biodegradability, and more eco-friendly exhaust gases [1]. Industrial biodiesel can be produced by a chemical reaction between triglycerides and low molecular weight alcohols, such as methanol or ethanol in the presence of a catalyst. A strong base, such as NaOH or KOH, is generally used to produce biodiesel since it is able to promote the reaction at relatively low temperatures [2]. However, the main drawbacks of homogeneous base catalysts are the large amount of waste water produced from the washing step and the high energy consumption for phase separation. These problems can be solved with the use of heterogeneous transesterification catalysts, which offer advantages such as prevention of side reactions and reusability of the catalysts.

A variety of solid catalysts—alkaline and alkaline earth metal oxides, various types of alkali metal compounds supported on alumina—has been examined for this reaction [3−5]. Higher amounts of alkaline will result in higher basic properties, which can promote the transesterification reaction. Zeolite is one of the most used catalysts because their basic properties are enhanced when alkali metal cations are exchanged with protons and bonded with the negatively charged framework [6,7]. KOH supported on NaY and NaX zeolite catalysts could prevent deactivation of the catalyst and performed as a heterogeneous-like system [7,8]. Additionally, mordenite has been explored as a catalyst for many reactions: modification of the alkalinity on the zeolite to enhance the electron density of the framework oxygen species and to promote the strength of molecular centers has been well documented in literature.

However, leaching of the active species into the solution during the course of a reaction has been reported [9]. Leaching affects significantly the industrial applications and extensive leaching threatens the reusability of the catalyst. In addition, one of the drawbacks of heterogeneous catalysts is the deactivation with time and the stability of the catalyst decreases slightly within the recycle run [10]. It has been reported that the deactivation mechanism of the heterogeneous catalysts for transesterification can be either the leaching of

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the active species or the adsorption of hydrocarbons onto the basic sites.

Taking this into account, the structure of mordenite is attractive to be used as a support. It is clear that the chemical composition and basic properties of the catalyst can play an important role in transesterification. Accordingly, KOH/mordenite could achieve a high conversion yield and high reusability, making it of interest to apply in biodiesel production. In the present study, the catalytic activities of KOH/mordenite in transesterification under mild conditions were determined in both a batch and a packed-bed reactor to evaluate the suitability of this catalyst. The influence of the basic properties and physical structure on the catalytic activity was also evaluated. Additionally, the reusability of KOH/mordenite was investigated.

2. Experimental

2.1. Materials

Refined palm oil was obtained from the Naval Engineering Command in Thailand. Mordenite zeolite was obtained from Zeolyst Company. Anhydrous methanol (Lab-Scan, 99.95%), potassium hydroxide (Lab-Scan), sodium sulfate (Fisher Scientific), and heptane (Fisher Scientific, puriss p.a., 99.5% GC) were used as chemicals for transesterification. Methyl heptadecanoate (puriss p.a., standard for GC, 99.7%) supplied by Fluka was used to measure the methyl ester content.

2.2. Catalyst preparation

The KOH/mordenite catalyst was prepared by an impregnation method. The pure mordenite zeolite was calcined at 600 °C for 3 h. To modify the mordenite zeolite with different amount of K loadings (5, 10, 15, 20, 25, and 30 wt%), the mordenite zeolite was impregnated with an aqueous solution of KOH for 24 h. Then it was dried at 110 °C for 24 h before use as a catalyst in the reaction.

2.3. Catalyst characterization

A Bruker X-ray diffractometer system (D8 Advance) equipped with a 2.2 kW Cu anode long fine focus ceramic X-ray tube for generating CuK_α radiation (1.5405 Å) was used as an X-ray source to obtain the XRD patterns at running conditions for the X-ray tube (40 kV and 40 mA). The detector scanned the intensity of diffracted radiation in the range of 10^o to 70^o (2θ) with a scan speed of 0.02^o (2θ)/0.5 s.

A scanning electron microscope (SEM), Hitachi/S-4800, was utilized to identify the microstructure and capture the micrograph of the catalyst morphology. The catalyst sample was placed on a stub and coated with platinum in a sputtering device before being placed in the sample holder of the SEM.

Specific surface area and pore volume were determined by physisorption of nitrogen at liquid temperature in a stationary mode using a Sorptomatic model 1990 instrument (Thermo Finnigan). Before analyzing, the volatile species adsorbed on the surface were eliminated by outgassing at 300 °C for 24 h. Helium gas was used as an adsorbate for blank analysis and nitrogen gas was used as the adsorbate for analysis. The specific surface area, pore volume, and pore size distribution were obtained by measuring the volume adsorbed at different P/P_0 values. Total pore volume was estimated by measuring the volume of the adsorbed gas at a P/P_0 of 0.99, and total micropore volume and micropore size distribution were obtained by applying the Horvath-Kawazoe method, 1983.

A Fourier transform infrared spectrophotometer (FTIR), Thermo Nicolet Nexus 670, was used to identify the chemical functional groups of the samples. The solid samples were ground into fine powder and mixed with potassium bromide (KBr) and pressed. The spectra were obtained at a resolution of 4 cm^{-1} in the range of 4000 cm^{-1} to 400 cm^{-1}.

The basic properties of the samples were determined using temperature-programmed desorption (Micromeristics 2900) of CO_2 (CO_2-TPD), which was used as the probe molecule. A 150 mg sample was degassed by heating in a flow of helium at a rate of 10 °C/min from room temperature to 500 °C for 1 h. After it was cooled to 50 °C, CO_2 gas was introduced for adsorption for 1 h. To remove the physically adsorbed CO_2 gas, the sample was purged with helium gas at a flow rate of 30 mL/min for 1 h. CO_2-TPD was performed at the rate of 5 °C/min from 30 °C to 600 °C.

Basic strength of the catalysts was determined using Hammett indicators of bromthymol blue ($H_- = 7.2$), phenolphthalein ($H_- = 9.8$), 2, 4-dinitroaniline ($H_- = 15.0$), and 4-nitroaniline ($H_- = 18.4$). An estimated titration method measured the total basic sites of the samples. Each catalyst sample (20 mg) was shaken in 5 mL of 0.02 M aqueous HCl for 1 h, and the remaining acid was then titrated with a standard base (0.02 M aqueous KOH).

Nuclear magnetic resonance (NMR) spectra were obtained by a Varian Inova model 400 spectrometer. ^{1}H, ^{27}Al, and ^{29}Si solid-state NMR were operated at frequencies of 400, 130.32, and 99.36 MHz, respectively, and were performed at room temperature with a spin rate of 10 kHz.

An energy dispersive X-ray fluorescence (XRF) spectrometer (Oxford model ED2000) was used to determine the bulk composition of each catalyst. The potassium contents of the fresh and spent catalysts were measured by XRF. The leached potassium was determined by the total amount of potassium that remained in the spent catalyst after being subtracted from the amount of potassium in the fresh catalyst.

Inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out with a Perkin-Elmer Optima 2100 DV (Wellesley, MA). The biodiesel was diluted with kerosene (0.1 g/g), and the glycerol was diluted with distilled water (0.01 g/g), following the method used by Yan et al. [11].