



Biodiesel production from transesterification of palm oil with methanol over CaO supported on bimodal meso-macroporous silica catalyst



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HIGHLIGHTS

- A series of CaO-loaded unimodal and bimodal porous silica catalysts were prepared.
- Basicity increased with increasing the amount of CaO content.
- The presence of macropores enhanced the accessibility of CaO inside the pellet.
- Bimodal catalyst exhibited a high %FAME with excellent regeneration efficiency.

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ABSTRACT

Calcium oxide-loaded porous materials have shown promise as catalysts in transesterification. However, the slow diffusion of bulky triglycerides through the pores limited the activity of calcium oxide (CaO). In this work, bimodal meso-macroporous silica was used as a support to enhance the accessibility of the CaO dispersed inside the pores. Unimodal porous silica having the identical mesopore diameter was employed for the purpose of comparison. Effects of CaO content and catalyst pellet size on the yield of fatty acid methyl esters (FAME) were investigated. The basic strength was found to increase with increasing the CaO content. The CaO-loaded bimodal porous silica catalyst with the pellet size of 325 μm achieved a high %FAME of 94.15 in the first cycle, and retained an excellent %FAME of 88.87 after five consecutive cycles.

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1. Introduction

Biodiesel is a biodegradable and non-toxic fuel derived from plant or algal oils and animal fats via transesterification, which is extensively accepted as a viable alternative to current petroleum-derived diesel (Luque et al., 2010). Homogeneous basic catalysts such as sodium and potassium hydroxides are commonly used in the industrial production of biodiesel (Vicente et al., 2004). However, using homogeneous catalysts has several disadvantages such as, corrosion problems, inability to reuse the catalysts and generation of large amount of wastewater (Ma and Hanna, 1999), which is

certainly to diminish their attractiveness associated with high reaction rate under mild reaction conditions.

Heterogeneous catalysts have the potential to address the disadvantage issues created by the conventional caustic homogeneous catalysts as they provide easier separation techniques, leave the product free of catalyst impurities and exclude the requirement for product neutralization and purification steps (Semwal et al., 2011). Furthermore, the lesser consumption of heterogeneous catalysts with reusability could potentially lead to economical production costs of biodiesel (Dossin et al., 2006; Mbaraka and Shanks, 2006).

A large variety of different heterogeneous catalysts have been investigated (Madhuvilakku and Piraman, 2013; Obadiah et al., 2012; Vieira et al., 2013). Among them CaO has been received much interest due to its mild reaction condition, relatively cheap and less impact on environment (Correia et al., 2014; Ho et al.,

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2012; Tang et al., 2013). Verziu et al. (2011) reported 92% yield of methyl esters in the transesterification of sunflower oil after 2 h at 75 °C with a 4:1 methanol to oil ratio and 1.4 wt% catalyst using thermally activated CaO catalyst. Kouzu et al. (2008) studied the CaO in the transesterification of refined soybean oil, using a 12:1 M ratio of methanol to oil, and obtained 93% yield of methyl esters after 1 h reaction time. However, partial dissolution of Ca^{2+} from the CaO surface does occur under reaction conditions, this contribution leads to the problem with separation of the Ca^{2+} from the products.

Supporting CaO on high surface area materials such as silica, alumina, and zinc oxide is found to be a good method to improve stability against the dissolution of Ca^{2+} (Albuquerque et al., 2008; Alba-Rubio et al., 2010; Umdu et al., 2009). The high surface area of the supports also allows a good dispersion of the metal oxide and thus increasing the catalytically active surface. Umdu et al. (2009) have investigated pure CaO and CaO supported on alumina in the transesterification of algal lipids to form biodiesel. The supported catalyst was found to be more active than pure CaO, which could be attributed to the much smaller CaO crystallite size of 5 nm formed on the support while the CaO crystallite size of the pure CaO was 164 nm. Albuquerque et al. (2008) firstly reported the use of CaO-loaded mesoporous silica (MCM-41 and SBA-15) as base catalysts for biodiesel production from sunflower oil. After 5 h, the biodiesel yield was found to be 95% by using 14 wt% CaO-loaded SBA-15 catalyst. Samart et al. (2010) used mesoporous silica as CaO support in the transesterification of soybean oil. The 95.2% yield of methyl esters is achieved after 8 h when using 15 wt% CaO-loaded mesoporous silica at 60 °C with 5 wt% catalyst and a 16:1 methanol: oil ratio. Although ordered mesoporous silicas (MCM-41 and SBA-15) derived catalysts have proven popular candidates for biodiesel production, these supports possess a two dimensionally ordered hexagonal arrangement of isolated 2.2–7.8 nm diameter parallel channels, leading to inefficient use of metal oxide dispersed inside the pores, resulting in low catalytic activity (Wilson and Lee, 2012; Witoon, 2012). Georgogianni et al. (2009) studied the transesterification reaction of rapeseed oil with methanol in the presence of either homogeneous or heterogeneous catalyst. The transesterification reaction using homogeneous catalyst was found to be 1–2 orders of magnitude higher when compared to that of the heterogeneous ones, which could be potentially explained by the diffusion constrains of the bulky rapeseed molecules into the relatively small pore of the solid catalysts.

Several attempts have been made to tailor catalyst porosity to minimizing mass transfer limitations of these bulky and viscous C16–C18 triglycerides of free fatty acids. In contrast to ordered mesoporous materials templated by surfactant micelles, mesoporous silica materials synthesized without template (silica xerogel) exhibited three dimensionally (3D) interconnected pore networks, which provided a greater accessibility through the open porous structure where active metal oxide could be anchored. In addition to 3D interconnected pore networks, the incorporation of macropores into mesoporous silica materials can significantly improve active site accessibility (Gheorghiu and Coppens, 2004; Witoon et al., 2011, 2013; Woodford et al., 2012).

In the present study, bimodal meso-macroporous silica material was synthesized and used as a CaO supported catalyst for the transesterification of palm oil with methanol. Unimodal mesoporous silica material having the identical mesopore diameter to bimodal meso-macroporous silica material has been prepared for the purpose of comparison. The physical properties of silica supports and CaO-loaded silica supports were characterized by means of N_2 adsorption-desorption, X-ray diffraction (XRD), scanning electron microscope (SEM), CO_2 temperature-programmed desorption (TPD) and X-ray fluorescence (XRF). The influences of the CaO

content and the pellet size of the catalysts on the yield of methyl esters were investigated.

2. Methods

2.1. Materials

Chitosan with 80% deacetylation was purchased from Eland Corporation. Calcium nitrate tetrahydrate, acetic acid, hydrochloric acid, and sodium hydroxide were purchased from Sigma-Aldrich Company. Sodium silicate ($\text{Na}_2\text{Si}_3\text{O}_7$: 30 wt% SiO_2 , 4 wt% NaOH) was obtained from Thai Silicate Company. All chemicals and reagents are of analytical grade and used without any further purification.

2.2. Preparation of unimodal and bimodal porous silica materials

Bimodal (meso-macro) porous silica was prepared via a sol-gel process using sodium silicate as a silica source and chitosan as a natural template. In a typical synthesis, 0.4 g chitosan was dissolved in 100 mL of 1% v/v acetic acid in deionized water at room temperature for 12 h. Then 5.5 g sodium silicate, primarily diluted with 10 mL deionized water, was slowly added to the chitosan solution under vigorous stirring. Afterwards, the pH value of the mixture was quickly adjusted to 6 by the addition of 2 M HCl or 2 M NaOH solution, respectively. The mixture was stirred at 40 °C for 3 h and after that it was poured into a Teflon container and aged in autoclave at 100 °C for 24 h. The obtained product was filtered, washed several times with deionized water, dried at 120 °C for 12 h and calcined at 800 °C for 4 h at a heating rate of 2 °C/min.

Unimodal porous silica having equivalent mesopore diameter to bimodal porous silica was synthesized using the similar condition as mentioned above except for the addition of chitosan.

2.3. Preparation of calcium oxide-loaded porous silica materials

Series of XCaO/U and XCaO/B catalysts were prepared by incipient wetness impregnation method, in which X was the amount of CaO content. The unimodal and bimodal porous silica supports were impregnated with the desired amount of calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) in aqueous solution. The slurry mixture was stirred at 60 °C for 1 h, dried at 120 °C for 12 h and calcined at 800 °C for 4 h at a heating rate of 2 °C/min.

2.4. Characterization

BET surface area and total pore volume of the samples were measured at -196 °C with a Quantachrome Autosorb-1C instrument (USA). Prior to measurements, the samples were degassed at 200 °C for 24 h. Pore size distributions of the samples were determined from the adsorption branch of the isotherms in accordance with the Barrett-Joyner-Hallenda (BJH) method (Gregg and Sing, 1982). The specific BET (S_{BET}) was estimated for P/P_0 values to be between 0.05 and 0.30. The total pore volume was measured at the relative pressure (P/P_0) of 0.995.

X-ray diffraction (XRD) patterns of the catalysts were attained on a diffractometer (Bruker D8 Advance) with $\text{Cu-K}\alpha$ radiation. The measurements were made at temperatures in a range of 15–70 °C on 2θ with a step size of 0.05°. The diffraction patterns were analyzed with the employment of the Joint Committee on Powder Diffraction Standards (JCPDS). The CaO crystallite size was calculated by means of the Scherrer Equation from the most intense CaO peak at 2θ of 37.4 as shown below (Patterson, 1939):

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