Biodiesel synthesis over millimetric γ-Al$_2$O$_3$/KI catalyst

Aminul Islam [a, b], Yun Hin Taufiq-Yap [a, b, *], Pogaku Ravindra [c], Siow Hwa Teo [a, b],
S. Sivasangar [a, b], Eng-Seng Chan [d, **]

[a] Department of Chemistry, Faculty of Science, University Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[b] Catalysis Science and Technology Research Centre, Faculty of Science, University Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[c] Centre of Materials and Minerals, School of Engineering and IT, Universiti Malaysia Sabah, 88999 Kota Kinabalu, Malaysia
[d] Chemical Engineering Discipline, School of Engineering, Monash University, Jalan Lagoon Selatan, 46150 Bandar Sunway, Selangor, Malaysia

ARTICLE INFO

ABSTRACT

The use of spherical millimetric gamma-alumina (γ-Al$_2$O$_3$) as a catalyst support for the production of biodiesel from palm oil was demonstrated. The catalyst support was produced using dripping method, and KI catalyst was loaded on the support using impregnation method. The highest FAME (fatty acid methyl ester) yield of 98% was obtained when the reaction was carried out under the conditions of catalyst to oil ratio of 0.6 g (4wt.%, $g_{cat.}/g_{oil}$) using 0.24 $g_{KI}/g_{\gamma\text{-}Al_2O_3}$ of catalyst loading, reaction time of 4 h, temperature of 60 °C and methanol to palm oil molar ratio of 14:1. XRD (X-ray diffraction) analysis showed the formation of K$_2$O and KAlO$_2$ phases on the KI/γ-Al$_2$O$_3$ catalyst which were possibly the active sites for the transesterification reaction. The highest number and strength of basic sites generated from the solid phase reaction of the KI/γ-Al$_2$O$_3$ catalyst loaded with 0.24 g kF/g γ-Al$_2$O$_3$ were confirmed by temperature programmed desorption of CO$_2$ (CO$_2$-TPD) analysis. The nitrogen adsorption−desorption isotherms was revealed a mesoporous structure of the catalysts. The leaching of potassium species in reused catalysts was observed, as verified by XRF (X-ray fluorescence). KI/γ-Al$_2$O$_3$ had a long life time and maintained sustained activity even after being repeatedly used for 11 cycles. The biodiesel yield was comparable to that produced from smaller catalysts. Thus, the catalyst could be potential for industrial use, as they can be handled safely, easily separated from the process fluid and used in fixed bed reactor to minimize pressure drop.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The most effective way to reduce CO$_2$ (carbon dioxide) emissions is to reduce fossil fuel consumption. Therefore, the biodiesel is gaining more attention as a carbon neutral source of energy. Recent research efforts have been directed towards the more economical and environmental friendly way to produce biodiesel using solid catalysts [1,2]. A number of studies have been focused on using solid basic or acidic catalyst for biodiesel production. Different types of powdered solid basic catalysts ordering on a micrometer scale have been studied, including KI/Al$_2$O$_3$ [3], CaO/KI/γ-Al$_2$O$_3$ [4]

KI/γ-Al$_2$O$_3$ [5], KOH/ZrO$_2$ [6], KNO$_3$/Al$_2$O$_3$ [7] and K/KOH/γ-Al$_2$O$_3$ [8]. Recently, the utilization of supported nano catalyst has been shown to be efficient for biodiesel production [9−11].

Despite the high percentage of FAME (fatty acid methyl ester) (>90%) achieved by powdered catalysts, many catalytic systems have not been commercialized because of the difficulties encountered when trying to separate such catalysts from the reaction media [12]. In addition, the small particle size gives rise to several problems such as high pressure drops, poor mass/heat transfer, poor contact efficiency and difficulties in handling and separation [13,14]. There are also possible health risks caused by inhalation of small particles. Therefore, the fabrication of catalyst with macroscopic form could be useful for industrial applications, as reported by Wang et al. [15].

One of the main reasons to consider heterogeneous catalysis for industrial processes is the ease of catalyst separation after the reaction. Separation processes represent more than half of the total investment in equipment for the chemical and fuel industries [16].

* Corresponding author. Department of Chemistry, Faculty of Science, University Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia. Tel.: +60 3 55145821; fax: +60 3 55146207.
** Corresponding author.
E-mail addresses: taufiq@upm.edu.my (Y.H. Taufiq-Yap), chan.eng.seng@monash.edu (E.-S. Chan).

Thus, the utilization of millimetric spherical catalyst support and their application in transesterification reactions will be a practical alternative to catalyst in powder form in view of following advantages; i) easy of separation of the catalyst by simple filtration, ii) the catalyst is easy to handle and reusable for several times. In addition, in the design of a catalyst, the shape should also be taken into account, as the shape preferably, spherical could minimize the abrasion of catalyst in the reaction medium [17]. In fact, the life time of the catalyst could be increased. Until now, the macroscopic (up to 1.0 mm in diameter) magnesia-rich magnesium aluminate spinel catalyst, such as $MgO \cdot MgAl_2O_4$ and $MgO/MgAl_2O_4/\gamma-Al_2O_3$ for biodiesel production have been reported by Wang et al. [15]. However, the biodiesel yield was still insufficient for practical applications. For instant, biodiesel yield obtained with the catalyst $MgO \cdot MgAl_2O_4$ and $MgO/MgAl_2O_4/\gamma-Al_2O_3$ were substantially low at 57% and 36% respectively in 10 h.

The aim of this work was to improve the biodiesel yield from transesterification of palm oil using a spherical millimetric gamma-alumina ($\gamma-Al_2O_3$) catalyst support. $\gamma-Al_2O_3$ was chosen because it can easily be synthesized, it possesses good support properties, and it is commercially available. KI (potassium iodide) was used as a model catalyst. The catalysts were prepared at different loading contents, and the effects of these catalysts on the transesterification reaction were evaluated in terms of the FAMEs yield. In addition, the characteristics of the synthesized catalysts, such as the morphological, structural, textural and base properties, were carried out using stereozoom microscopy, XRD (X-ray diffraction), N_2 adsorption/desorption isotherms and CO_2-TPD (temperature-programmed reduction) techniques. A screening of the reaction conditions has been carried out by examining the effects of reaction time, methanol to oil molar ratio and the calcination temperature of catalyst. Besides, the relationship between the basicity of the catalyst and their catalytic activity in the transesterification of palm oil was also discussed. Finally, the reusability of the catalyst was determined and the leachate of catalyst into the reaction product was verified by XRF (X-ray fluorescence).

2. Materials and methods

2.1. Materials

Boehmite (AlOOH) in a powder form was provided by BASF Catalysis LLC, USA. Reagents used during catalyst synthesis were: hydrochloric acid, HCl (JT Baker, Mexico), ammonia solution (System ChemAR, Malaysia), paraffin oil (870 g/mL density at 20 °C, Ajax chemicals, Australia) and potassium iodide, KI (Sigma-Aldrich, GmbH, Germany). Commercial edible grade palm oil was purchased from a local store (Lam soon edible oil, Malaysia). Methanol (Labscan Asia Co. Ltd. Thailand) was used for the transesterification reactions and hexane was purchased from Fisher Scientific, UK. Methyl heptadecanoate (internal standard for gas chromatography) and standard references for fatty acid methyl ester analysis were supplied by Fluka Analytical (Buchs, Switzerland).

2.2. Preparation of catalyst

Spherical millimetric gamma-alumina ($\gamma-Al_2O_3$) support was prepared using oil drop granulation method described in previous publications [18–20]. Spherical millimetric gamma-alumina ($\gamma-Al_2O_3$) support was prepared using a sol–gel process previously described by Wang et al. [18]. The boehmite powder (300 g/L) was suspended in deionized water and dispersed ultrasonically by a sonicator. The sonication process took place for 3 min at amplitude of 70%. The pH of the resulting boehmite suspension prior to drop formation was then adjusted to 1.0 by addition of an appropriate amount of 1N HCl, where the sol turned to a gel. The gel was then transferred dropwise by a pump at a constant flow rate (0.5 mL/min) into a liquid column consisting of paraffin oil at the upper layer and ammonia solution at the bottom layer (Fig. 1). Droplets of boehmite gel were formed due to the surface tension effect during transiting through the oil layer and the gel droplets were further aged in the ammonia solution for 1 h. The paraffin solution column was 25 cm in height, which provided enough time for the gel drops to form spherical particles [19,20]. During aging, ammonia would neutralize the acid in the wet-gel beads and thus, the wet-gel droplets became rigid. Then, the beads were then dried in the air at room temperature (25 °C) for 12 h and were later calcined at 800 °C for 3 h. The calcined beads were then impregnated with an aqueous solution of KI (potassium iodide), as shown in Table 1. Finally, the bead-supported catalysts were calcined at 500 °C for 3 h to make the catalyst active for transesterification reaction.

2.3. Catalyst characterization

The shape and size analysis of the support beads were carried out by analyzing the digital images captured by a digital camera (Moticam-350, version 2.0 ML, China) installed on a stereozoom microscope (Stemi DV4, Carl Zeiss, Germany) using image analyzer (SigmaScan Pro 5.0, SPSS Inc). In order to measure the shape of the bead quantitatively, SF (sphericity factor) was used. It express the divergence of a particle shape from spherical [21], where the value zero indicates a perfect sphere and higher values indicate a greater degree of shape distortion. SF was calculated according to eq. (1):

$$SF = (D_{max} - D_{per})/(D_{max} + D_{per}) \tag{1}$$

where D_{max} is the maximum diameter passing through a bead centroid (mm), and D_{per} is the diameter perpendicular to D_{max} passing through the bead centroid (mm).

The crystal structure of the catalyst was determined by Shimadzu diffractometer model XRD-6000 using Cu-Ka radiation. The samples were scanned from 10 to 70° with a speed of 0.05 s^{-1}. The peaks were analyzed with the DiffracPlus software and the phases were identified by the PDF (powder diffraction file) database (JCPDS, International Centre for Diffraction Data).

The basicity of the catalyst was determined by temperature programmed desorption of CO_2, as described by Islam et al. [17]. The experiments were performed by loading the samples (100 mg) in the Thermo Finnigan TPD/R/O 1100 series catalytic surface analyzer connected to a thermal conductivity detector. The samples were preheated to 800 °C under a flowing stream of helium for 30 min (10 °C min^{-1}, 30 mL min^{-1}). Then, the temperature was decreased to 30 °C under a CO_2 flow for 1 h (30 mL min^{-1}) at which the adsorption of CO_2 will be carried out. Subsequently, the sample was flushed with helium at 30 °C for 30 min in order to remove any physisorbed molecules from the samples prior to the CO_2 desorption analysis. The desorption of CO_2 was carried out by heating the sample up to 800 °C under a helium flow (10 °C min^{-1}, 30 mL min^{-1}) and the amount of desorbed CO_2 was detected and determined using a thermal conductivity detector.

The surface area and pore structure of catalysts were determined at liquid nitrogen temperature (−196 °C) with a Sorptomatic 1990 (Thermo Finnigan Italia S.P.A) instrument. Prior to the measurements, the samples were degassed at 150 °C under vacuum conditions until static vacuum was reached. The BET (Brunauer, Emmett and Teller) method was used to measure the surface area of the catalysts. The BJH (Barrett, Joyner and Halenda) method was employed to measure the pore distribution from the desorption isotherm. The pore volume was calculated according to the