Transesterification of waste cooking palm oil by MnZr with supported alumina as a potential heterogeneous catalyst

CrossMark

H. Amani [a], Z. Ahmad [a], M. Asif [b], B.H. Hameed [a],*

[a] School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia
[b] Chemical Engineering Department, College of Engineering, King Saud University, P. O. Box 800, Riyadh 11421, Saudi Arabia

A B S T R A C T

The transesterification of waste cooking palm oil (WCPO) with methanol into fatty acid methyl esters (FAMEs) was investigated using solid acidic mixed oxide catalysts $Mn_{3.5x}Zr_{0.5y}Al_xO_3$ prepared via coprecipitation. The effects of reaction temperature, time, molar methanol-to-oil ratio, and catalyst loading were investigated. The stability of the catalytic activity was examined via leaching and reusability tests through five consecutive batch runs. The catalyst achieved a FAME content of more than 93%, and the optimal reaction conditions are as follows: reaction temperature of 150 °C, reaction time of 5 h, molar methanol-to-WCPO ratio of 14:1, and catalyst loading of 2.5 wt.%.

© 2014 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

1. Introduction

Vegetable oils are one of the common feedstock for the oleochemical industry. The properties of vegetable oils differ among different sources [1–3]. However, they share the same general individual components of free fatty acids (FFAs) and generally contain water in different proportions, depending on the oil source [4]. Investing on inexpensive triglyceride resources and efforts to reduce the amounts of reagents should be considered. Researchers are actively investigating methods to eliminate or reduce these problems or drawbacks [5]. The ultimate aim is generally to produce a high-quality product at an optimum rate with economic process [6]. Non-edible vegetable oils such as crude palm, crude Jatropha, and karanja are suitable for transesterification reaction [7–10]. These oils are not useable for human consumption due to presence of some toxic components. Furthermore, used cooking oils from deep frying have been used as a potential feedstock for biodiesel production [11].

Transesterification is the most popular way to transform vegetable oils or animal fats into biofuels [12]. Methanol is the most commonly used alcohol for producing biodiesel according to its relatively cost advantage and shorter carbon chain [13]. This reaction can be catalyzed by basic or acidic catalysts. However, basic catalysts provide higher reaction rates, whereas acid catalysts are

preferred when significant amounts of impurities are present in the reactants [14].

In recent years, researchers have shifted toward developing sustainable solid acid catalysts for transesterification reaction that are insensitive to the FFA in the feedstock and, subsequently, easy to separate from the reaction products [15–17]. Solid acid catalysts such as $Ni/Al_2O_3–ZrO_2$ [18], sulfonic ion-exchange resin [19], TPW/SiO_2 [20], and zeolite solid acid catalyst [21] have been successfully used in the transesterification reaction of different triglyceride sources. In the heterogeneous catalysis field, problems with solubility and low surface area of the active species in the reaction mixture are the main reasons for the immobilization of the active acidic component on appropriate porous support materials. The supported catalyst should offer the stability of a heterogeneous catalyst while providing a suitable surface area for active components and also promote the reaction with the same activity of homogenous catalysts [22].

The adible oiles are usable for human consumption. moreover, waste cooking oils (WCO) from deep frying have been used as a economical feedstock for biodiesel production. In this work, solid mixed-oxide acid catalysts of $Mn_{3.5x}Zr_{0.5y}Al_xO_3$ ($0.1 \le x \le 0.5$, $0.5 \le y \le 2.5$) were synthesized, characterized, and assayed for its ability to catalyze the transesterification of waste cooking palm oil (WCPO). The reaction was investigated for a wide range of parameters, and the catalyst was tested for possible leaching and potential reusability. The present work will contribute to the field of heterogeneous catalysts which could be used to transform the widespread feedstock mainly waste cooking palm oil into valuable and ecofriendly energy resources.

* Corresponding author. Fax: +60 45941013.
  E-mail address: chbassim@eng.usm.my (B. Hameed).

2. Materials and methods

2.1. Materials

WCPO was collected from a cafeteria in the Engineering Campus of the Universiti Sains Malaysia (USM). The raw WCPO was filtered to remove all insoluble impurities and then heated at 100 °C for 2 h to remove all the moisture. The acid value of the WCPO was 2.45 mg KOH g^{-1} and its water content was 0.08 (w/w). The catalysts were synthesized from analytical grade $Mn(NO_3)_2 \cdot 4H_2O$, $ZrOCl_2 \cdot 8H_2O$, Al $(NO_3)_3$ $9H_2O$, NH_4OH, and 65% HNO_3 solution purchased from Merck Co. (Malaysia). The methanol used for the transesterification reactions and the n-hexane used as a solvent for gas chromatography (GC) analysis were also purchased from the same company. The GC reference standards for fatty acid methyl esters (FAMEs) were purchased from Sigma–Aldrich Co. (Malaysia).

2.2. Catalyst synthesis

The heterogeneous mixed oxide catalysts, with empirical formula of $Mn_{3.5x}$ $Zr_{0.5y}$ Al_xO_3 with different Mn:Zr:Al atomic ratios ($0.1 \leq x \leq 0.5$, and $0.5 \leq y \leq 2.5$), were prepared via coprecipitation. Briefly, for a particular batch, the calculated amounts of $ZrOCl_2 \cdot 8H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ were mixed with 10 mL NH_4 OH in water until the pH reached 10 (the amount of metal components were changed at different x and y values). The obtained metal hydroxide precipitate was filtered, washed with water, and dried overnight at 110 °C. Before using the solid catalysts in the transesterification reaction, the dried catalyst was calcined at different temperatures (300–500 °C) and durations (3–6 h) to determine the best calcination conditions. Similarly, $Mn_{3.5x}Zr_{0.5y}O_3$ catalyst was prepared with precipitation method and the activity was tested to compare the effect of including aluminum during the transesterification reaction.

2.3. Catalyst characterization

The Brunauer–Emmet–Teller (BET) surface area, pore size distribution, and pore volume properties of the catalysts were measured from the nitrogen adsorption–desorption isotherms using Micrometrics ASAP 2020 V3.02 H. The powder X-ray diffraction (XRD) patterns of the catalysts were determined on a diffractometer D8 Advanced Bruker AXS 203–39D X-Ray solution (model Philips PW1710), and the measurements were conducted from $2\theta = 10°$ to $2\theta = 90°$. The acidity of the catalysts was determined using NH_3 temperature-programmed desorption (TPD). High-resolution transmission electron micrographs of catalysts were obtained using a 200 kV TECNAI G 20 S-TWIN FEI field emission equipped with an EDAX system.

2.4. Transesterification reaction

A stainless steel, Teflon-lined autoclave batch reactor (250 mL) equipped with a magnetic stirrer was used for the transesterification reaction of WCPO with methanol. Typically, 80 mL of WCPO, 40 mL of methanol, and 1.77 g of catalyst were placed inside a reactor with reaction duration of 5 h at 150 °C (5 °C/min heating rate). Constant stirring at 500 rpm was used to minimize mass transfer limitations. The reaction time was counted when the reaction temperature reached the desired temperature. After the desired reaction time, the reactor was quickly cooled to ambient temperature, and the catalyst was separated from the product mixture via centrifugation. The FAMEs was analyzed via gas GC (Shimadzu 2010 Plus, Japan) equipped with flame ionization detectors (FID-2010 Plus) and capillary column (Nukol; 15 m length, 0.53 mm internal diameter, and 0.5 μm film thickness). Methyl

heptadecanoate was used as the internal standard. Then, for each transesterification reaction one sample (1 μL) was injected and FAME content was calculated using the following equation [23]:

$$FAME\% = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100$$

$\sum A$ Total peak area of the methyl ester in C_{14} to that in $C_{24:1}$;
A_{EI} Peak corresponding to methyl heptadecanoate;
C_{EI} Concentration of the methyl heptadecanoate solution ($mg\,mL^{-1}$);
V_{EI} Volume of the methyl heptadecanoate solution (mL);
M Mass of the sample (mg).

2.5. Catalyst reusability and stability

To examine catalyst reusability, the catalyst was separated from the reaction mixture (transesterification reaction of WCPO under optimum conditions) by filtration, washed with methanol and hexan, dried at 110 °C for 2 h. The catalyst was reused in the next run without further treatment. To assess catalyst stability, the optimum amount of catalyst (1.77 g) was stirred with 40 mL of methanol at 150 °C for 5 h. After catalyst recovery, methanol was mixed with 80 mL of WCPO, and the reaction was carried out under the optimum conditions (150 °C for 5 h).

3. Results and discussion

3.1. Catalyst characterization

The textural parameters, including surface area, pore volume, and pore size of $Mn_{1.4}Zr_{0.35}O_3$ and $Mn_{1.4}Zr_{0.35}Al_{0.6}O_3$ catalysts are summarized in Table 1. The $Mn_{1.4}Zr_{0.35}Al_{0.6}O_3$ catalyst has higher pore volume and surface area. In this study, alumina was used to improve the surface area of the catalyst and form a composite structure with other metal oxides. The modification of the surface and textural properties has significant affect on the catalysts activity. Cannilla et al. studied the sunflower oil transesterification reaction to produce biodiesel in the present of Mn-based catalysts. Different elemental composition has changed the texturat properties and basic sits density which has agreement with this work [24]. Also, the XRD was performed on the $Mn_{1.4}Zr_{0.35}O_3$ and $Mn_{1.4}Zr_{0.35}Al_{0.6}O_3$ catalysts to identify their phase and crystalline structure (Fig. 1). The $Mn_{1.4}Zr_{0.35}Al_{0.6}O_3$ mixed oxide exhibited the cubic phase of Mn_3O_4, Mn_5O_8, ZrO_2, $ZrMn_2O$, and at $2\theta = 36.8°$, 28.5°, 31.3°, 53.8°, 82.3° and 59.7°. Additional phases were observed clearly in the diffraction patterns of the modified sample ($Mn_{1.4}Zr_{0.35}Al_{0.6}O_3$) for cubic phase of $Al_3Zr_2O_2$, $Mn_{3.85}$ $Al_{11}O_2$, and Al_2O_3 at $2\theta = 38.3°$, 58.6°, 33.8°, and 57.16°. As it is mentioned, by aluminum addition there will be a rise in the reductions in the diffraction peaks of the support in XRD patterns. The difference in the mean pore diameter of the support and the diameter of the $Mn_{1.4}Zr_{0.35}O_3$ pertains to this good dispersion whereby allows for a more uniformed distribution of $Mn_{1.4}Zr_{0.35}O_3$ on the alumina surface. Similar results has been observed for MgZnO supported on alumina [25], and cobalt doped MgO [26].

The acidity of the prepared mixed oxide catalysts ($Mn_{1.4}Zr_{0.35}O_3$ and $Mn_{1.4}Zr_{0.35}Al_{0.6}O_3$) was investigated using NH_3-TPD analysis. Fig. 2 shows the recorded and total acid site concentrations. NH_3 gas

Table 1
Textural parameters of the $Mn_{1.4}Zr_{0.35}O_3$ and $Mn_{1.4}Zr_{0.35}Al_{0.6}O_3$ catalysts.

Characteristic	$Mn_{1.4}Zr_{0.35}O_3$	$Mn_{1.4}Zr_{0.35}Al_{0.6}O_3$
BET surface area ($m^2\,g^{-1}$)	170.11	196.00
Total pore volume ($cm^3\,g^{-1}$)	0.15	0.20
Average pore diameter (nm)	3.63	4.10