



Chromium–tungsten heterogeneous catalyst for esterification of palm fatty acid distillate to fatty acid methyl ester



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ARTICLE INFO

Article history:

Received 5 October 2014

Revised 11 March 2015

Accepted 15 March 2015

Available online 8 April 2015

Keywords:

Palm fatty acid distillate

Solid catalyst

Methyl ester

Metal oxides

ABSTRACT

Chromium–tungsten mixed oxides heterogeneous catalysts were prepared and evaluated in the esterification of palm fatty acid distillate (PFAD) to produce fatty acid methyl ester (FAME). The reactions were conducted in a batch reactor at temperature range of 110–190 °C and catalysts were characterized by BET, SEM, TEM, FTIR and XRD. The effects of catalyst preparation conditions (metal ratio, calcination temperature and time), the influence of reaction conditions (temperature and time, methanol/PFAD molar ratio, catalyst dosage) and catalyst stability were studied. The prepared catalyst with formula CrWO₂ (calcined at 600 °C for 3 h) gave the maximum FAME content of 86% at best reaction conditions (170 °C; 3 h, 2:1 methanol/PFAD molar ratio; 1.5 wt.% catalyst dosages) and can be recycled for several times. Thus, CrWO₂ has good potentials as heterogeneous catalyst for FAME synthesis from high acid value oils.

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1. Introduction

Biodiesel is a clean-burning renewable fuel that has become important alternative to petroleum diesel due to depletion of fossil fuel reserves and environmental concern. It consists of fatty acid methyl esters (FAME) produced commonly from natural triglycerides such as palm oil, soybean oil and rapeseed oil [1–3]. The high cost of edible plant oils is the main drawback in biodiesel commercialization as the feedstock cost contributes largely to the overall production cost. Many low cost feedstocks were used such as waste oils and non-edible plant oils, but their sustainability is a major challenge due to limited quantity of generation [4,5].

Palm fatty acid distillate (PFAD) is a low value by-product obtained during the fatty acid stripping and deodorization stages of crude palm oil physical refining process. Thus, PFAD is sold cheaper compared to refined oils. It is composed of about 85% free fatty acids (FFA) and remaining other substances such as triglycerides, glycerides and sterols [6]. Malaysia as one of the biggest exporter of palm oil in the world, also produces large amount of PFAD from palm oil industries. PFAD is generally used for non-food applications such as manufacturing of candles and fuel in industrial boilers. This useful and low cost raw material is a promising sustainable source of feedstock for esterification process to produce FAME, which typically use homogeneous acid catalyst. The drawbacks are their solubility in reaction mixture that contributes to costly separation process, environmental

hazards, equipment corrosion and non-reusable [7]. Alternatively, heterogeneous catalyst has been reported to overcome these problems in terms of simplified downstream separation and purification process, catalyst reusability and eco-friendly nature. Several works reported tungstated catalysts to be active for FAME synthesis under specific conditions. Jacobson et al. [8] reported modification of zirconia–alumina with tungsten oxide, which provides high mechanical strength and enhances the acidity of the catalyst. Furuta et al. [9] reported tungstated zirconia–alumina has higher activity than sulfated zirconia–alumina but high reaction temperature (250 °C) and long reaction time (20 h) were required to obtain 90% conversion. Tungsten oxide zirconia was reported to have better activity and stability compared to sulfated zirconia with over 90% FAME conversion without leaching of tungsten in the esterification of used vegetable oils [10]. Although these catalysts reported high activity, some require energy intensive operating conditions such as high temperature and long reaction time. Considering the good potential of tungsten oxide catalysts in FAME synthesis from high FAA oils, it is of great benefit to investigate its activity in esterification of PFAD under moderate conditions.

In this work, chromium–tungsten mixed oxides heterogeneous catalysts were prepared via sol–gel method. Catalysts based on chromium oxide were used in several catalytic reactions. CuCr₂O₄ has shown high catalytic activity in the hydrogenation of glycerol [11]. Chromium oxide supported on zirconium-doped silica catalyst was active in the dehydrogenation of propane [12]. Hence, the objective of this work is to evaluate the feasibility of using the new solid catalyst to synthesize FAME from PFAD. The parameters in catalyst

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Table 1
BET surface area, total pore volume, average pore diameter, surface acidity and FAME content for various synthesized catalysts.

Catalyst chemical formula	Cr:W ratio by mass	Surface area ^a (m ² /g)	Pore volume ^a (mm ³ /g)	Pore size ^a (Å)	Acidity ^b (μmol/g)	FAME content (%)
CrWO ₂	1:1	3.11	10.25	190.95	487	85.78
CrW ₂ O ₂	1:2	2.22	7.23	131.18	415	78.06
Cr ₂ WO ₂	2:1	8.53	25.92	121.51	389	75.50
WO ₂	0:1	12.87	57.35	178.20	310	65.72
CrO ₂	1:0	15.29	57.58	150.65	338	63.92

^a Obtained from N₂ adsorption–desorption.

^b Obtained from chemical titration method.

preparation conditions such as metal ratios, calcination temperature and time as well as the effect of reaction conditions such as reaction temperature and time, methanol to PFAD molar ratio, catalyst dosage and catalyst stability were studied.

2. Material and methods

2.1. Materials and chemicals

PFAD (195 mg KOH/g acid value, 0.85% water content) was purchased from IOI Oleochemical Industries Berhad in Penang, Malaysia. Cr(NO₃)₃·9H₂O and WCl₆ used as precursor for Cr and W, respectively were purchased from Merck (Malaysia). Methanol (purity 99%) used for esterification and methyl heptadecanoate (purity 99.5%) used as internal standard for gas chromatography (GC) analysis were purchased from Merck (Malaysia) and Sigma–Aldrich (Malaysia), respectively. Hexane (purity 96%) used as solvent for GC, ethanol (purity 99%) and HNO₃ (purity 65%) used for the catalyst preparation were purchased from Merck (Malaysia). All the chemicals used were analytical reagent grade.

2.2. Catalyst preparation

The catalysts with chemical formula of Cr_xW_yO₂ with various Cr: W ratio by mass (0 ≤ x ≤ 2; 0 ≤ y ≤ 2) were prepared via sol–gel method. For a typical catalyst preparation process: 5.8 g of Cr(NO₃)₃·9H₂O and 1.6 g of WCl₆ were dissolved separately in 5 mL of distilled water. Each solution is then slowly added to a beaker containing 40 mL of ethanol and 1 mL of HNO₃. The solution was allowed to stir for 4 h at 40 °C on a magnetic stirring hot plate and then left for 24 h aging process until gel was formed. The sample is dried in an oven for 12 h at 95 °C, followed by calcinations in air using a muffle furnace at a desired temperature (ranging from 300 °C to 700 °C) and time (ranging from 1 h to 5 h).

2.3. Catalyst characterization

Fourier transform infrared (FTIR) was used to determine the active surface functional groups using a Nicolet, Thermo Scientific instrument (spectra range 4000–400/cm). Philips XL30S scanning electron microscope (SEM) was used for catalyst morphology analysis. The sample placed on aluminum stub for electron reflection and vacuumed for 5–10 min before analysis. Phillips electron-microscope-CM12 with image analyzer was used for the transmission electron microscopy (TEM) analysis. The sample was dispersed in ethanol prior to analysis. The catalyst specific surface area, pore volume and pore size distribution properties were obtained by nitrogen adsorption/desorption at 77 K on ASAP 2020 Micromeritics instrument, using the Brunauer Emmett–Teller (BET) method. Powder X-ray diffraction (XRD) patterns on Phillips PW 1710 diffractometer with Cu Kα radiation at 40 kV and 40 mA was used to determine the catalyst structural characteristic. The catalyst surface acidity was determined using the chemical titration method, whereby 1 g of catalyst is added to 25 mL

0.1 M HCl solution and vigorously stirred for 24 h at room temperature. The solid phase is filtered and the solution is then titrated with 0.1 M NaOH solution with phenolphthalein indicator [13].

2.4. Esterification of PFAD and FAME analysis

The esterification of PFAD was conducted in a 100 mL stainless steel batch reactor with a four-bladed pitched turbine impeller and a thermocouple. The semi-solid PFAD was preheated in an oven at 80 °C to liquefy it. In a typical procedure, 39.5 mL of PFAD, 10.6 mL of methanol and 0.53 g of catalyst were charged into the reactor and mixing commenced immediately to ensure contact between the reactants. The reactor temperature was controlled at the desired temperature (ranging from 110 °C to 190 °C) by a heater with a programmable PID temperature controller and it is self-pressurized from 10 to 15 bar. The stirrer was increased to a maximum speed of 500 rpm, to sufficiently keep the system uniform in temperature and suspension and to avoid mass transfer limitations. The molar ratio of methanol to PFAD ranged from 1:1 to 6:1, while the amount of catalyst varied from 1.0 wt.% to 6.0 wt.% of the PFAD. After desired reaction time (1–6 h), the heater was switched off and the reactor was immediately cooled to room temperature by quenching in cold water bath. The catalyst was then separated from the product mixture by centrifugation. The products were collected and left to settle for 12 h to separate into FAME (top layer) and water (bottom layer).

The FAME content was measured by gas chromatography (GC) analysis using a GC2010 Shimadzu instrument equipped with flame ionization detector (FID). Nukol fused silica capillary column (15 m in length, 0.53 mm internal diameter and 0.5 μm film thicknesses) was used. The FAME was analyzed by dissolving 20 μL sample into 250 μL methyl heptadecanoate internal standard. Injection volume of 1 μL was used in the GC and the FAME obtained was calculated using the EN14103 application note [14].

2.5. Catalyst recycling

Upon completion of the 1st cycle reaction, the solid catalyst was recovered by filtration and washed thoroughly with methanol to remove the remaining residues of reactants and products on its surface. The catalyst was dried in an oven at 100 °C for 12 h before use in the subsequent cycle with fresh reactants to study its reusability. The regeneration study was conducted similarly, but the catalyst was re-calcined at best conditions of 600 °C for 3 h before use in the subsequent reaction cycles. The leaching study was conducted by contacting the catalyst with methanol for 3 h at 170 °C and used the filtrate in the reaction with PFAD.

3. Results and discussion

3.1. Characterization of catalysts

The surface area, pore volume, average pore size and acidity of the prepared catalysts calcined at constant calcination temperature and time but consist of various Cr: W ratios that are shown in Table 1. It is

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