Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–9

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Effect of alumina loading on the properties and activity of SO_4^{2-}/ZrO_2 for biodiesel production: Process optimization via response surface methodology

Behgam Rahmani Vahid[a,b], Naser Saghatoleslami[a,c], Hamed Nayebzadeh[a,*], Javad Toghiani[d]

[a] Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, P.O. Box 9177948974, Mashhad, Iran
[b] Department of Chemical Engineering, Esfarayen University of Technology, Esfarayen, North Khorasan, Iran
[c] Department of Petroleum Engineering, Eqbal Institute of Higher Education, Mashhad, Iran
[d] Faculty of Chemical Engineering, Sahand University of Technology, P.O. Box 51335-1996, Sahand New Town, Tabriz, Iran

ARTICLE INFO

Article history:
Received 14 July 2017
Revised 19 October 2017
Accepted 8 December 2017
Available online xxx

Keywords:
Biodiesel
Alumina
Sulfated zirconia
Waste cooking oil (WCO)
Response surface methodology (RSM)

ABSTRACT

The key challenges for the production of biodiesel are the utilization of cheap oils, such as waste cooking oil (WCO), and insensitive and active heterogeneous catalysts. Therefore, in this study, an alumina-supported sulfated zirconia (SZ) nanocatalyst was synthesized using the solvent-free method and the effect of the optimal percentage of aluminum precursor (Al-P) was examined on its activity in the transesterification of WCO to biodiesel. The catalysts were characterized by XRD, FT-IR, BET surface area, and TEM analyses, and their acidity was determined by the NaOH titration method. The results revealed that SZ supported with 25 mol% of Al-P has the best catalytic properties due to its highest fraction of tetragonal phases of zirconia and lowest crystalline size, well bonded sulfate groups with zirconium and aluminum ions and highest acidity. Moreover, the transmission electron microscopy (TEM) images confirmed the reduction of particle size in SZ from ≈25 nm to ≈7 nm by the loading of alumina. Then, transesterification reaction parameters and their interactions were evaluated and optimized using the response surface methodology (RSM). The statistical analysis explained that reaction temperature and time have the most influence on the conversion of WCO. In addition, the interaction of reaction temperature with methanol/WCO ratio and time affected the biodiesel process. The optimum reaction parameters were obtained as 148.5 °C, 2.9 wt.% of the catalyst, 12.7 molar ratios of methanol/WCO, and reaction time of 93 min. The yield of 93.5% was attained and the nanocatalyst preserved its activity for at least four times with an only ≈10% reduction in the conversion.

1. Introduction

As a result of global warming and air pollution, authorities seek to reduce the use of petroleum fuels [1,2]. Biodiesel is an attractive alternative fuel produced from the reaction of triglycerides or free fatty acids with an alcohol in the presence of a catalyst [3,4]. Although homogeneous catalysts such as NaOH and KOH are widely used for the production of biodiesel [5], they are not suitable for oils with high amounts of free fatty acids (FFAs) such as WCO [6]. Therefore, concern has been raised for the utilization of solid acid catalysts due to environmental problems and the formation of by-product using homogeneous catalysts [7,8].

Zirconia exhibits a high activity for esterification and transesterification reactions due to its amphoteric properties. In order to improve the catalytic activity, a wide range of catalysts were employed for supporting zirconia [9–11]. The sulfate group showed a high ability for improving the activity of zirconia for esterification reaction [12,13]. However, SZ has certain drawbacks. For example, it is deactivated after each reaction and is not easily regenerated by simple re-calcination in air [14]. Therefore, the use of different metal oxides for reinforcing SZ and enhancing catalytic activity and reusability is economically significant in mass usage [15,16]. Ye et al. [17] utilized molybdenum (Mo) to support SZ that zirconia modified by 5% sulfate and 5% Mo presented optimal catalytic performance. Sani et al. [18] investigated the activity and catalytic performance of Yb–SZ for biodiesel production and found that SZ doped by Yb has a significantly higher activity than SZ. Yu et al. studied the influence of SZ promoted by rare Earth oxide and alumina [19]. They reported that Yb_2O_3-Al_2O_3-promoted SZ exhibits the highest activity in the esterification reaction. Moreover, Komintarachat et al. [20] evaluated the capacity of porous

* Corresponding author.
E-mail address: hamed.nayebzadeh@mail.um.ac.ir (H. Nayebzadeh).

https://doi.org/10.1016/j.jtice.2017.12.007
1876-1070/

Please cite this article as: B. Rahmani Vahid et al., Effect of alumina loading on the properties and activity of SO_4^{2-}/ZrO_2 for biodiesel production: Process optimization via response surface methodology, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2017.12.007

support materials such as alumina, silica, titania, and zinc oxide, for WO_x-synthesized catalysts based on FAME yield. The results revealed that Al_2O_3 has a higher ability as a porous material due to its higher surface area. Alumina was extensively examined for esterification and transesterification reactions [21–23]. The effect of alumina loading on the activity of SZ in the esterification of oleic acid to methyl oleate was presented in our previous study [24]. However, no data are available in the literatures on the optimum amount of alumina needed for loading on SZ to obtain the highest activity and reusability.

Among the suggested methods for the preparation of nanocatalysts with high activity and reusability such as precipitation-reduction [25], impregnation [26], and combustion [27], the solvent-free method suggested by Sun et al. [28] presents a simple rout, a well-crystalline final catalyst, good distribution of particle size, and high activity and reusability, especially in the biodiesel production process. Garcia et al. [29] reported that SZ synthesized by the above method has a higher activity compared to the co-precipitation and impregnation method in the transesterification reaction. This method was also considered by other researchers with acceptable results for biodiesel production [30–32]. Therefore, it seems that the solvent-free method is a simple and suitable method for synthesizing nanoscale materials.

It must be noted that parameters such as reaction temperature, molar ratio of alcohol/feedstock, catalyst concentration, and reaction time affect the biodiesel yield. In comparison with unplanned approaches, the statistical design of experiments helps researchers gain a better insight into the interactions among experimental variables; offers a better understanding of the process; and reduces research time and costs [33].

Therefore, the aim of this study was to investigate the effect of different amounts of Al-P loading on SZ to obtain higher activity and reusability. The catalysts prepared by solvent-free method were characterized by X-ray powder diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area, Fourier-transform infra-red (FT-IR), and TEM analyses. After assessing their acidity using the NaOH titration method, their activity was examined in the transesterification reaction. Finally, the process conditions for the maximum fatty acid methyl ester (FAME) content in the presence of optimum SZ promoted by Al-P were optimized using the response surface method (RSM), and the reusability of the optimum nanocatalyst was evaluated.

2. Materials and method

2.1. Materials

WCO was supplied from Nan Razavi Co. (Mashhad, Iran). It was severely purified from solid suspense particles using two-step filtration and was then heated for 2 h at 120 °C to remove moisture. The average molecular weight of WCO was obtained at 962 g/gmol based on the acid value (3.25 mg KOH/g) and saponification value (178.118 mg KOH/g).

$ZrOCl_2{\cdot}8H_2O$ and methyl heptadecanoate were purchased from Sigma Aldrich Co. and high-purity $(NH_4)_2SO_4$, $Al_2(SO_4)_3{\cdot}18H_2O$, methanol, ethanol, KOH, NaOH, and n-heptan were obtained from Merck Co.

2.2. Catalyst preparation

SZ was prepared as suggested by Sun et al. [28] with some improvements. The SZ supported by alumina was prepared by grinding $ZrOCl_2{\cdot}8H_2O$ (5 g) with $(NH_4)_2SO_4$ (12.30 g) and Al_2 $(SO_4)_3{\cdot}18H_2O$ (2.327 to 4.655 mmol as 0.15 to 30 mol% of $ZrOCl_2{\cdot}8H_2O$) in a ceramic mortar for 20 min. Afterwards, it was placed at room temperature for 18 h, followed by calcination at 500 °C for 5 h [24]. The samples were labeled as 0.15A/SZ, 0.20A/SZ, 0.25A/SZ, and 0.30A/SZ.

2.3. Catalyst characterization

Phase identification and crystalline size were determined by X-ray diffraction method with UNISANTIS/XMP 300 by means of Cu Kα radiation at 45 kV and 80 mA. Crystalline size was then calculated from the Scherrer's equation. The BET surface area, pore volume, and average pore size of the synthesis catalysts were measured by the BET method using an AUTOSORB 1 of QUANTACHROME Company (U.S.A.). The FTIR spectroscopy measurements were performed by mixing samples into KBr pellets on a SHIMADZU 4300 spectrometer in the range of 400–4000 cm^{-1}. In order to determine the catalyst acidity defined as mmol of NaOH per g of catalyst [34], 0.2 g of the catalyst solution in 10 mL of deionized water was titrated by 0.1 M NaOH solution. Furthermore, particle size was estimated using the TEM technique by a LEO 912AB TEM.

2.4. Catalyst testing

To assess the catalytic activity, the transesterification reaction of WCO and methanol was carried out in a stainless steel batch reactor (100 mL). The reaction was carried out at 120 °C for 90 min with 15 molar ratio of methanol/WCO and 3 wt.% of catalyst. Then, the catalyst and glycerol were simply separated from the product mixtures by filtration and decanter, respectively. Biodiesel was gradually heated in order to eliminate the excess methanol and water.

The FAME content in biodiesel samples was measured using a gas chromatograph (Teif Gostar Faraz Co., Iran) equipped with a flame ionization detector (FID) and a capillary column (CP SIL 5cb, 30 mm × 0.25 mm × 0.25 µm). Helium gas at the rate of 25 mL/min and methyl heptadecanoate were employed as the carrier gas and internal standard [35]. Approximately 250 mg of the sample was weighed in a 10 mL vial. Then, 5 mL of the methyl heptadecanoate solution (10 mg/mL) was added using a pipette, and the injected volume of this sample to GC was 1 µL. The ester content (biodiesel) (C) was expressed as a mass fraction in percentage and calculated using the following formula:

$$C = \frac{(\Sigma A) - AEI}{AEI} \times \frac{CEI \times VEI}{m} \times 100\%$$

ΣA is the total peak area from the FAME C14:0 to C24:1;
AEI is the peak area of methyl heptadecanoate;
CEI is the concentration (mg/mL) of the methyl heptadecanoate solution;
VEI is the volume (mL) of the methyl heptadecanoate solution;
m is the mass (mg) of the sample.

2.5. Experimental design and statistical analysis

In this study, a central composite design (CCD) combined by RSM was used for the optimization of four independent variables. The encoded and actual levels of the independent variables are listed in Table 1. A mathematical model, describing the relationship between the predicted response variable (FAME content) and the reaction conditions in second-order equation was developed based on the Design-Expert software. As cited in the literature, the second-order polynomial equation provides the fitting of the experimental results, as shown in the below equation [36]:

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i_i>j}^{k} \sum_{j}^{k} b_{ij} X_i X_j + e \quad K = 4 \qquad (1)$$

Please cite this article as: B. Rahmani Vahid et al., Effect of alumina loading on the properties and activity of SO_4^{2-}/ZrO_2 for biodiesel production: Process optimization via response surface methodology, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2017.12.007