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ScienceDirect

Energy Procedia 138 (2017) 75–80

Energy Procedia

www.elsevier.com/locate/procedia

2017 International Conference on Alternative Energy in Developing Countries and Emerging Economies 2017 AEDCEE, 25 - 26 May 2017, Bangkok, Thailand

Comparison in Catalytic Activities of Sulfated Cobalt-Tin and Sulfated Aluminium-Tin Mixed Oxides for Esterification of Free Fatty Acids to Produce Methyl Esters

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Abstract

In this study, sulfated tin oxide was modified with cobalt oxide and aluminium oxide resulting in sulfated cobalt-tin (SO_4^{2-}/Co_2O_3-SnO_2) and sulfated aluminium-tin (SO_4^{2-}/Al_2O_3-SnO_2) mixed oxide catalysts, respectively. Their catalytic activities for esterification of free fatty acids (FFA) in crude palm oil were investigated. Cobalt-tin and aluminium-tin mixed oxides were prepared by co-precipitation method. The mixed oxides were further impregnated with sulfate ions by immersing in sulfuric acid solution, dried and calcined at 450-500 °C. The properties of SO_4^{2-}/Co_2O_3-SnO_2 and SO_4^{2-}/Al_2O_3-SnO_2 samples were determined by nitrogen adsorption, X-ray diffraction and potentiometric titration. The activities of SO_4^{2-}/Co_2O_3-SnO_2 and SO_4^{2-}/Al_2O_3-SnO_2 catalysts were tested in a stirred-tank reactor equipped with a reflux condenser. Esterification between crude palm oil containing 10-10.2 wt% of FFA and methanol was carried out at various reaction times. The comparison in the catalytic activities of SO_4^{2-}/Co_2O_3-SnO_2 and SO_4^{2-}/Al_2O_3-SnO_2 was made. The results showed that the SO_4^{2-}/Al_2O_3-SnO_2 had higher catalytic activity than SO_4^{2-}/Co_2O_3-SnO_2 in esterification of FFA to produce methyl esters.

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Keywords: Biodiesel; Esterification; Sulfated tin oxide; Crude palm oil; Free fatty acid

1. Introduction

Biodiesel (or alkyl esters) is a renewable energy and can be biologically degradable. It can fulfill energy security needs without sacrificing engine's operational performance [1]. Although biodiesel is technically feasible and environmentally beneficial, not all feedstocks are economically competitive [2]. The main disadvantage regarding biodiesel production is the high cost of oil feedstocks. Therefore, low-quality oils containing large amounts of free fatty acids (FFA) are required. However, the biodiesel production from low-quality oils requires two consequent processes, esterification and transesterification, in order to avoid soap formation and obtain a considerable yield of biodiesel in the following alkaline catalyzed transesterification. In the esterification step, FFA must be converted to their alkyl esters (biodiesel) in the presence of an acid catalyst. Typically, FFA must be esterified to an acceptable level, e.g. 1 wt% [3] or 1 vol% [4]. A suitable heterogeneous acid catalyst is preferred to a conventional

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Peer-review under responsibility of the scientific committee of the 2017 International Conference on Alternative Energy in Developing Countries and Emerging Economies.
10.1016/j.egypro.2017.10.058

homogeneous acid catalyst such as H_2SO_4 for the esterification because heterogeneous catalysts are easily separated from the reaction mixture and recycled. The biodiesel production process therefore is simplified. Unlike a homogeneous acid catalyst, the use of a heterogeneous acid catalyst does not require neutralization of the remaining acid. Moreover, heterogeneous acid catalysts such as sulfated metal oxides are less corrosive and toxic than conventional acids. Therefore, reactor corrosion is reduced.

Sulfated tin oxide (SO_4^{2-}/SnO_2) is a promising catalyst in a sulfated metal oxides family for esterification reactions due to its very high acidity, which is called superacidity [5]. SO_4^{2-}/SnO_2 has been described to have higher acid strength than sulfated zirconia, SO_4^{2-}/ZrO_2 [5,6], which well catalyzes esterification reactions of carboxylic acids [7,8]. Therefore, the activity of SO_4^{2-}/SnO_2 is expected to be greater than SO_4^{2-}/ZrO_2. However, the studies on the structure and applications of SO_4^{2-}/SnO_2 are relatively few, compared to SO_4^{2-}/ZrO_2 and other SO_4^{2-}/M_xO_y-type solid superacids [9]. Moreover, SO_4^{2-}/SnO_2 is not commercially available, unlike SO_4^{2-}/ZrO_2. With these reasons, more attentions should be focused on SO_4^{2-}/SnO_2.

Khder et al. [10] and Moreno et al. [11] have performed intensive studies in the production and characterization of SO_4^{2-}/SnO_2 as well as its catalytic activity for esterification reactions. The catalytic activity of SO_4^{2-}/SnO_2 has been found to strongly depend on its acidity. Such acidity is greatly influenced by the concentration of sulfates and calcination temperature. The maximum activity was obtained when the SO_4^{2-}/SnO_2 catalyst contained 30 wt% sulfates and was calcined at 550 °C, giving about 92% conversion of acetic acid [10]. In the esterification of oleic acid with ethanol, the highest activity of SO_4^{2-}/SnO_2 catalyst occurred when it contained 0.3 wt% sulfates and was calcined at 500 °C, giving 49% conversion of oleic acid [11]. However, the modification of SO_4^{2-}/SnO_2 with other metal oxides is hardly found in the literature. For example, the introduction of Al_2O_3 onto SO_4^{2-}/SnO_2 creating sulfated aluminium-tin mixed oxide (SO_4^{2-}/Al_2O_3-SnO_2) has been reported by Guo et al. [9]. Heiba et al. [12] has investigated the structure of the mixed oxides, $SnO_2 + xAl_2O_3$ (x = 0, 25, 50, 75 wt%) synthesized by sol-gel technique. Another example of SO_4^{2-}/Al_2O_3-SnO_2 for acylation was carried out by Zhao et al. [13]. Introducing Al_2O_3 to SO_4^{2-}/SnO_2 offers the benefit of cost saving. Different sources of Al lead to different catalytic activities of the SO_4^{2-}/Al_2O_3-SnO_2 [14].

Sulfated tin oxide can also be modified with cobalt oxide resulting in sulfated cobalt-tin mixed oxide (SO_4^{2-}/Co_2O_3-SnO_2) catalyst. The SO_4^{2-}/Co_2O_3-SnO_2 has been reported to have higher catalytic activity than SO_4^{2-}/SnO_2 for direct oxidation of *n*-heptane to ester [15]. The SO_4^{2-}/Co_2O_3-SnO_2 could catalyze esterification reaction due to the presence of Lewis and Brönsted acid sites in its structure [16].

In this study, sulfated tin oxide was modified with cobalt oxide and aluminium oxide resulting in sulfated cobalt-tin (SO_4^{2-}/Co_2O_3-SnO_2) and sulfated aluminium-tin (SO_4^{2-}/Al_2O_3-SnO_2) mixed oxide catalysts. Their activities for esterification of FFA in crude palm oil were investigated. Cobalt-tin and aluminium-tin mixed oxides were prepared with co-precipitation method. The mixed oxides were further impregnated with sulfate ions. The properties of SO_4^{2-}/Co_2O_3-SnO_2 and SO_4^{2-}/Al_2O_3-SnO_2 were determined with nitrogen adsorption, X-ray diffraction and potentiometric titration. The activities of SO_4^{2-}/Co_2O_3-SnO_2 and SO_4^{2-}/Al_2O_3-SnO_2 catalysts were tested in a stirred-tank reactor equipped with a reflux condenser. Esterification between crude palm oil containing 10-10.2 wt% of FFA and methanol was carried out up to 4 hours. Palm oil is an abundant resource in Southeast Asian countries; therefore, it is an economic and commercially feasible feedstock for biodiesel production.

2. Experimental

2.1. Preparation of catalysts

Sulfated cobalt-tin (SO_4^{2-}/Co_2O_3-SnO_2) and sulfated aluminium-tin (SO_4^{2-}/Al_2O_3-SnO_2) mixed oxide catalysts were synthesized by adjusting a two-step method proposed by Furuta et al. [17]. In the first step, the mixture of cobalt (or aluminum) and tin hydroxides was synthesized with co-precipitation method. 10 g of $SnCl_4.5H_2O$ and the required amounts of $CoCl_2.6H_2O$ or $AlCl_3$ (corresponding to 10 mol% Co and 10 mol% Al, respectively) were dissolved in distilled water. The ammonia solution was added to the mixed solution with stirring until the pH was 8. The precipitated product was separated, suspended in 4 wt% CH_3COONH_4, filtered and dried at 100-105 °C for 24 h, yielding cobalt-tin or aluminium-tin hydroxides. In the second step, the compounds were immersed in H_2SO_4 solution (1 mol/L). The gel was stirred for 1 h, filtered, dried at 100-105 °C for 2 h and calcined at 450 °C (for cobalt-tin gel) and 500 °C (for aluminium-tin gel) for 3 h.

2.2. Characterization of catalysts

Sulfated cobalt-tin and sulfated aluminium-tin mixed oxide samples were characterized with X-ray diffractometer (JEOL JDX 3530) with Cu Kα radiation. The 2θ was scanned in the range of 20–60°. Nitrogen adsorption at -196 °C was employed using Quantachrome Autosorb Automated Gas Sorption System to determine adsorption isotherms, BET specific surface areas, pore volumes and average pore sizes of the samples. Non-aqueous potentiometric titration was used to measure the acidities of sulfated cobalt-tin and sulfated aluminium-tin mixed oxide samples according to the procedure proposed by Khder et al. [10].

2.3. Esterification of FFA in crude palm oil

Catalytic activities of SO_4^{2-}/Co_2O_3-SnO_2 and SO_4^{2-}/Al_2O_3-SnO_2 for esterification of FFA in crude palm oil to produce methyl esters were evaluated in a round bottom flask fitted with a magnetic stirrer and a reflux condenser. A mixture of 25 ml of crude

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