

Alternative Production of Fatty Acid Methyl Esters from Triglycerides using Sulphated Zirconia

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Abstract

Sulphated zirconia (SZ) was synthesized using two different methods with the same molar ratio (1:6) of reactants: (1) the direct mixing of $ZrOCl_2 \cdot 8H_2O$ and $(NH_4)_2SO_4$, designated as SZ₁; and (2) via the conventional wet-precipitation method with a molar ratio of 1:6 rather than the conventional 15 ml H_2SO_4 to 1g of $Zr(OH)_4$, denoted by (SZ₂). The catalysts physiochemical properties were precisely characterized by FTIR, SEM, X-ray diffraction, EDX, XPS, and Py-DRIFTS techniques. The two methods of preparation with same molar ratio of sulphating agents led to sulphated zirconias that exhibited different morphological and structural properties in terms of specific surface areas, thermal stability, acid sites, and surface sulphate. The catalysts activity was tested in thermocatalytic cracking of triglyceride; a direct conversion process for fatty acid methyl esters (biodiesel). The SZ₁ not only exhibited higher conversion of triglycerides but higher fatty acid methyl esters (FAMES) yields of approximately 59% after 3h as compared to SZ₂ (32%). In addition the sulphated zirconia, SZ₁ was selective towards unsaturated esters whereas SZ₂ was selective towards saturated esters.

Keywords: Sulphated zirconia, Catalyst preparation, Thermocatalytic cracking, FAMES

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Introduction

The use of vegetable oil in the production of biodiesel by transesterification with alcohol has been exploited with methanol being the most widely used. Transesterification relies on the use of either strong base or strong acid homogeneous catalysts for effective performance, but homogeneous catalysts are associated with a variety of technical hurdles that limit their use for biodiesel production and may eventually cause the demise of the process. Transesterification requires the use of high quality virgin oil or feedstock below 0.5wt % free fatty acid (Chen *et al.*, 2007). This could result into the formation of soap instead of the desired biodiesel, additional processing time and cost. Several methods have been reported to tackle these problems such as the use of enzymes (Fukuda *et al.*, 2001) and liquid acid catalysts (Serio *et al.*, 2008). However the high cost of enzymes and corrosion caused by liquid acid have hindered their usage. Although there have been recent developments in heterogeneous catalysis for biodiesel production by transesterification (Yan *et al.*, 2010), the separation of methyl ester (FAMES) from crude glycerol, alcohol recovery, and intolerance to free fatty acid (FFA) greater than 3.5% in feedstocks are still major hindrances associated with this traditional method of biodiesel production. To overcome these limitations of transesterification and sustain biodiesel

production, a possible alternative could be the use of solid acid catalysts in thermocatalytic cracking. A direct conversion process, which could completely eliminate all the existing limitations and offers several advantages such as simplified flow sheet without the use of alcohol, thereby reducing capital costs, additional gaseous product streams and importantly no glycerol in the product stream. Recently Yan *et al.* (2010) reported advances in heterogeneous catalysis for biodiesel production. Among many heterogeneous solid acid catalysts, sulphated zirconia has proved to be promising and has been extensively exploited for many organic reactions (Katada *et al.*, 2000; Furuta *et al.*, 2004). However it has been found to possess relatively low surface area and known to suffer leaching in the presence of polar solvents such as methanol (Hino and Arata, 1994). Most authors reported sulphated zirconia as having more Lewis acid sites than Brønsted acid site (Morterra *et al.*, 1994). It implies there is need for more research in terms of increased stability of acid sites to avoid leaching, thermal stability, enhancement of mass transfer to avoiding diffusion limitations. The aim of the present study is to further improve the surface area and increase the active acid sites of sulphated zirconia catalyst via preparation method. Hence, the solvent-free and conventional wet-precipitation methods with same molar ratio of reactants were used, characterized and their catalytic activity was compared in