

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 SZ_1 ; and (2) the conventional wet-precipitation method denoted by (SZ_2). The catalysts physicochemical 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 SZ_1 not only exhibited higher conversion of triglycerides but higher fatty acid methyl esters (FAMES) yields of approximately 59% after 3h as compared to SZ_2 (32%). In addition the sulphated zirconia, SZ_1 was selective towards unsaturated esters whereas SZ_2 was selective towards saturated esters.

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

1. Introduction

Currently the world is becoming increasingly environmentally aware, and renewable fuels such as biodiesel are becoming increasingly prevalent. The use of vegetable oil in the production of biodiesel by transesterification with alcohol has been exploited with methanol being the most widely used (Serio et al., 2008). Transesterification relies on the use of either strong base or strong acid homogeneous catalysts for effective performance. 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. 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 limited 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 level of free fatty acid (FFA) greater than 3.5% in feedstocks are still major hindrances associated with transesterification. In order to overcome these limitations 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, and importantly no glycerol in the product stream. Among the 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). This, of course, is not surprising since sulphated zirconia had already

been described as a super-acid catalyst with an acidity 10^4 times stronger than that of 100% sulphuric acid (Hino et al., 1979; Katada et al., 2000). Though it possesses a relatively small surface area, of which several authors have reported that its catalytic properties are a strong function of the preparation method used (Yamaguchi, 1990; Yadav and Nair, 1999). Since then, most research has focused on synthesizing sulphated zirconia through different routes, starting materials and conditions (Yamaguchi, 1990; Davis et al., 1994). The aim of the present study therefore is to further improve on the properties of the catalyst as well as the active acid sites for thermocatalytic reaction of triglycerides. The objectives of this work were to synthesize sulphated zirconia (SZ) catalysts via the solvent-free and conventional wet-precipitation methods with same molar ratio of reactants, and to compare the catalytic activity in thermocatalytic cracking of triglycerides for the production of fatty acid methyl esters (biodiesel).

2. Experimental

The SZ₁ was prepared via solvent free technique as described by Sun et al., (2005): Briefly, ZrOCl₂.8H₂O (99.5%, Sigma-Aldrich) and ammonium sulphate (NH₄)₂SO₄ (99%, Sigma-Aldrich) were weighed into a mortar at a molar ratio of 1: 6 and ground for 20 minutes. The mixture was allowed to age for 18 h before calcination at 600°C under air flow for 5 h. The conventional sulphated zirconia (SZ₂) was also prepared using a molar ratio of 1:6 of zirconium hydroxide to sulphuric acid. The surface areas were obtained from N₂ adsorption/desorption isotherms determined at 77K using the Coulter™ (SA 3100™ series). The samples were outgassed for 2 h at 200°C prior to the analysis. The XRDP was

performed using a Panalytical X'Pert Pro Multipurpose Diffractometer (MPD) fitted with an X'Celerator and a secondary monochromator. The diffractograms were recorded from 2°C to 100°C using Cu K α radiation with a wavelength of $\lambda = 1.54$ generated at 40 kV and 40 mA from 2°C to 100°C. Elemental composition was investigated using energy dispersive X-ray (EDX). Pyridine-DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) was used to determine the acids site on the catalysts after pyridine adsorption. Samples were diluted in KBr (5% dilution) to avoid absorption saturation at low wave numbers. Thermogravimetric (TGA) analysis (Pyris STA 6000 Model) was used to monitor the sulphate content on the catalysts as a function of mass loss with respect to temperature, in flowing helium of 30 ml/min with temperature rate 10°C/min in 30–900°C temperature range. The catalysts were tested in a thermocatalytic reaction carried out in a 100ml (Model: 4560) batch reactor equipped with a magnetic stirrer and an external heating mantle. The reaction was performed using rapeseed oil at 270°C and conversion monitored against time for 3 h. The liquid product was analysed using BS EN 14105: 2003 on a Perkin Elmer GCMS (Clarus) 600/560D) equipped with a capillary column (15m×0.25mm, i.d. 0.25 μ m film thickness), and helium as the carrier gas. FAMES were determined and quantified according to BS EN 14103:2003 on Hewlett Packard 5890 gas chromatograph with an FID detector. The column temperature was 210°C while the FID and injector were at 250°C each.

3. Results and Discussion

The sulphur content in the catalysts was initially estimated using infrared (IR) spectroscopy. Comparing the intensities of the absorbance of both

catalysts, as shown in Figure 1, the SZ₁ catalyst has approximately twice the quantity of sulphate ions than the SZ₂.

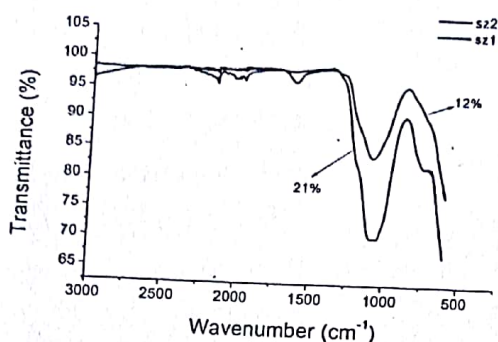


Fig. 1: The FTIR spectra of both catalysts from the different methods of preparation

This is an indication that more sulphate ions were retained on the surface of the SZ₁ catalyst by the solvent-free method than that of SZ₂, however, the sulphur species observed was similar. The surface acidity was determined using infrared spectra of the adsorbed pyridine on the catalysts, results obtained revealed the presence of both Lewis and Brønsted acid sites with different intensities. From the IR of adsorbed pyridine, Brønsted and Lewis acid sites on SZ₂ are 53% and 47% compared to the SZ₁, having approximately 60% and 40% of Brønsted and Lewis acid respectively. However, and interestingly, the SZ₂ catalyst has about 6% more Brønsted acid sites than Lewis acid sites. However, other studies (Corma et al., 1994; Farcasiu et al 1997; Hino et al., 2006) reported sulphated zirconia catalyst as having mainly Lewis acid sites when prepared by the conventional method. Studies of their XPS spectra of S2p showed an increased presence of surface sulphate on the SZ₁ catalyst. Deconvoluting the peaks revealed that the spectra of S2p are of two species; the protonated and

deprotonated at 169.5eV and 171eV, respectively. On the other hand the O1s spectra of SZ₁ and SZ₂ showed a pronounced asymmetry of peaks at 530.5eV and 532.5eV. The O1s peak of SZ₂ indicates approximately a 1:1 ratio of sulphate and oxide oxygen peaks while the SZ₁ catalyst from the solvent-free method exhibited only a very small (15%) shoulder at binding energy 530.5eV corresponding to the oxide oxygen of the zirconia (Figure 2).

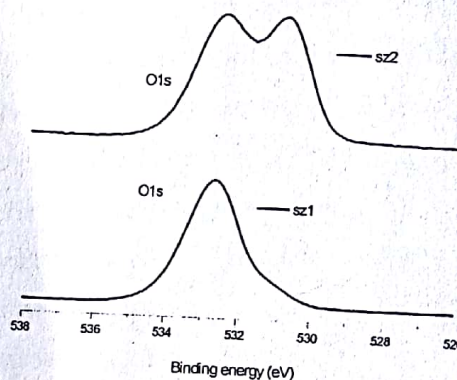


Fig. 2: XPS spectra of O 1s of SZ₁ and SZ₂ catalysts

This implies that the surface of SZ₁ catalyst has more sulphate oxide than zirconia oxide. It was further confirmed by the weight percentage of sulphur on the catalysts according to their elemental analysis (EDX) (Table 1). The textural properties are as given in Table 1 and shown in Figure 3.

Table 1: Textural Properties and Elemental Analysis of the SZ₁ and SZ₂ Catalysts

Catalyst	BET (m ² /g)	Crystallite size (nm)	Elemental analysis (wt%)			
			Zr	O	S	Zr/S
SZ ₂	79	17.3 ^{T,M}	48.2	47.3	4.5	10.7
SZ ₁	168	A	35.5	51.6	12.9	2.75

T = tetragonal phase, A = amorphous, M = monoclinic

In a previous report, the conventional wet-precipitated sulphated zirconia (using ratio 1:15) had a surface area of 65m²/g (Eterigho et al., 2011). The increased surface area implies more area available for reaction.

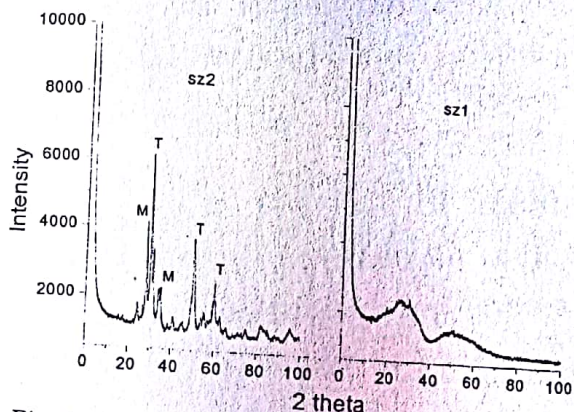


Fig.3: XRD showing the difference phases of the SZ₁ and SZ₂ catalysts

This agrees with the findings of Farcasiu et al.(1997) where a low sulphate load could result in the appearance of the monoclinic phase. It is worth adding that the XRD of the starting reactant, Zr(OH)₄ for both catalysts was amorphous in nature. The sulphate on the surface of the catalysts was further monitored by a thermogravimetric analysis (TGA) and the profile is shown in Figure 4. It

reveals three distinct peaks based on weight loss. The first peak at 200°C is an indication of desorption of adsorbed water. This was also reported by Strydom and Pretorius (1993) and Hino et al. (2006). The second stage at 600 to 800°C represents the loss of sulphates from the surface of the catalysts; it is interesting to note that SZ₁ experienced a greater loss (39%) than the SZ₂ (13%). The last stage from 800°C represents the gradual decomposition of zirconium sulphate to zirconia and gas.

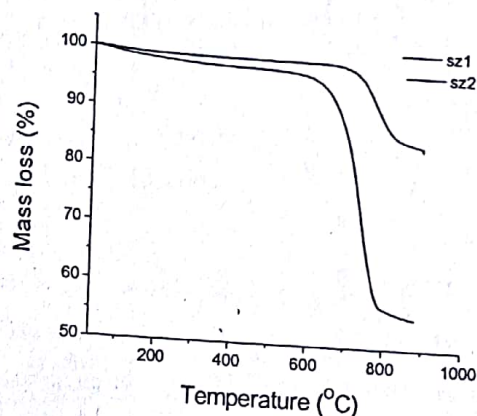


Fig.4: Thermogravimetric analyses (TGA) of SZ₁ and SZ₂

Both catalysts were active in cracking triglycerides for the production of fatty acid methyl esters amongst other products. The triglyceride conversion for SZ₁(65%) was greater than that of SZ₂(57%) after 3h. SZ₁ exhibited greater purity for fatty acid methyl esters (FAMEs) of approximately 59% and 32% for SZ₂ in the product mixture and selectively, SZ₁ FAMEs comprised of more unsaturated esters than SZ₂ which had more of saturated esters as seen in Figure 5 (a & b).

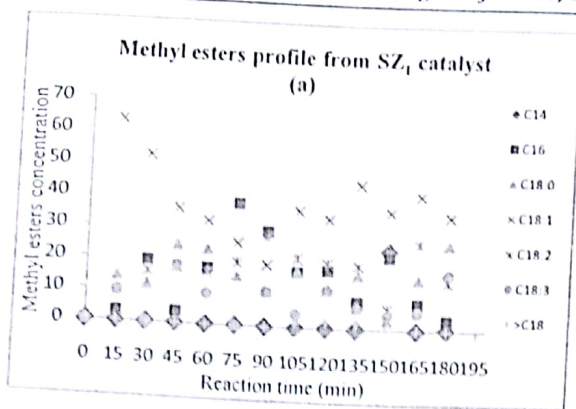


Fig.5a: FAMEs profile from SZ₁ showing saturated, mono and poly unsaturated esters

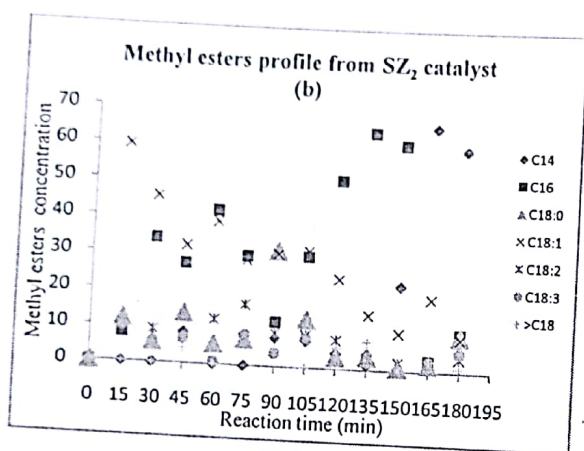


Fig.5b: FAMEs profile from SZ₂ showing saturated, mono and poly unsaturated esters

4. Conclusions

The synthesis of active crystalline and amorphous sulphated zirconias from different methods of preparation using the same molar ratio of sulphating agent was achieved. Based on the results of various analyses conducted on the prepared catalysts, sample SZ₁ proved to be better than sample SZ₂ in terms of catalytic activity for fatty acid methyl acid production (FAMEs). The selectivity towards unsaturated esters could only be explained by the presence of higher percentage of sulphate on the surface of the SZ₁ catalyst. The

unique selectivity for saturated and unsaturated esters may be a significant process advantage of this form of catalyst.

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