



Short Communication

Triglyceride cracking for biofuel production using a directly synthesised sulphated zirconia catalyst

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ABSTRACT

In this study, sulphated zirconia was directly synthesised and compared to the conventional wet method of preparation. The surface areas and pore sizes were $169 \text{ m}^2/\text{g}$, $0.61 \mu\text{m}$ (directly synthesized) and $65 \text{ m}^2/\text{g}$, $0.24 \mu\text{m}$ (conventional method), respectively. Directly synthesized sulphated zirconia was amorphous, whereas conventionally prepared sulphated zirconia is polycrystalline. Their IR spectra were broadly similar, although the area of the 1250 to 950 cm^{-1} band was larger for directly synthesised sulphated zirconia. Not only were conversions greater for directly synthesised sulphated zirconia (63% vs. 42% after 4 h), but it exhibited significantly greater yield for fatty acid methyl esters. The percentage yield (after 1 h) of methyl esters was 43% for the directly synthesised catalyst and 15% for the conventionally synthesised.

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1. Introduction

Biofuel can be defined as liquid or gaseous transport fuels that are produced from biomass substrates or bioresource (Michael, 2008). Among the biofuels, a significant amount of attention has been directed to biodiesel. This is a fatty acid methyl ester (FAME) produced by transesterification of triglycerides using monohydric alcohols in the presence of an alkaline catalyst (Meher et al., 2006). The predominant base-catalysed process is prone to unwanted side reactions, leading to downstream separation problems. Several methods have been proposed to tackle these problems, among which are the use of enzymes, acid catalysts and pre-esterification with acid catalysts. Recently, the use of heterogeneous catalysts in thermochemical cracking to produce biofuels has begun to gain attention. In terms of maximizing the profitability of this process, the choice of catalyst is paramount, as the type of fuel and yield is a strong function of the catalyst (Ooi et al., 2005). However, challenges to development of viable heterogeneous catalysts are enormous. Research in recent years has shown the role of preparation on catalytic properties of catalysts; as a result, various methods of preparation of solid catalysts for biofuel production have been reported. Kirszensztejn et al. (2009) investigated the use of alumina and its modified form in cracking rapeseed oil. A mixture of water, carbon dioxide, hydrogen, aliphatic was aromatic was produced. They observed that the preparation method of the modified catalyst led to consider-

able variation in the surface area of the catalyst and in turn the yield of the product.

Sulphated zirconia has been the subject of much attention as a well-characterised super-acid catalyst for organic reactions. Yadav and Nair (1999) reviewed conventional methods of preparation of sulphated zirconia (see Table 1 below). Although sulphated zirconia has the highest acidity amongst known solid super-acids, it is susceptible to leaching, rapid deactivation and a relatively small surface area (Sun et al., 2005). Therefore a considerable amount of research has focused on improvement of its catalytic activity and stability.

Yadav and Murkute (2004) published using chlorosulphonic acid as a precursor, in an organic solvent rather than the conventional sulphuric acid impregnation. The catalyst was found to exhibit higher catalytic activity for esterification than the conventionally prepared sulphated zirconia. Yi et al. (2005) used zirconium nitrate and ammonium sulphate in an alcoholic medium at a 393 K. The resulting sulphated zirconia was crystalline, tetragonal, high surface area.

Clearly extensive research has been performed on heterogeneous acid catalysts. However, there are few publications on the use of heterogeneous acid catalysts in thermocatalytic cracking for biodiesel production. Likewise, the use of sulphated zirconia in cracking has been widely studied, but little has been reported on its use in thermocatalytic cracking of triglycerides. Rattanaphra et al. (2010) reported the use of sulphated zirconias prepared via solvent-free method for transesterification of triglycerides. However less is known about directly synthesised sulphated zirconia in thermocatalytic cracking of triglycerides for biodiesel production. Therefore, the objective of this study is to synthesize

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Table 1
Various conventional procedures for the preparation of sulphated zirconia (Yadav and Nair, 1999).

Starting material	Precipitating agent	Sulphating agent	Calcination temperature (°C)	Nature of phases ^a		Surface area (m ² /g)
ZrOCl ₂ · 8H ₂ O/ZrO(NO ₃) ₂	Liq. NH ₃	H ₂ SO ₄ /(NH ₄) ₂ SO ₄	350	M	A	–
			650	M	T	–
ZrCl ₄	Urea	H ₂ SO ₄ /(NH ₄) ₂ SO ₄	850	M	T + M	–
			200	A	A	241
	Liq. NH ₃	H ₂ SO ₄ /(NH ₄) ₂ SO ₄	400	M	A + C	115
			600	M + C	A + C	19.6
ZrOCl ₂ · 8H ₂ O	Liq. NH ₃	H ₂ SO ₄	650	T		34

^a A: amorphous; M: monoclinic; C: cubic; T: tetragonal.

sulphated zirconias by direct synthesis, in addition to the conventional wet method, and to compare their catalytic activities in thermocatalytic cracking of triglycerides at low temperature of 270 °C.

2. Methods

2.1. Materials and equipment

All the chemicals were purchased from Sigma–Aldrich and Fisher Scientific. Rapeseed oil was from Henry Colbeck Ltd., UK. Environmental Scanning Electron Microscopy (ESEM; Model: XL30), ImageJ software, Coulter™ SA 3100™ series, X-ray diffractometer (Siemens D5000) and Fourier Transform Infrared Spectroscopy (FTIR Varian 800; Scimitar series) were used for characterization.

2.2. Catalyst preparation

Sulphated zirconia catalysts were synthesized in two ways: (i) the “conventional” method and (ii) “direct synthesis”.

2.2.1. Preparation of sulphated zirconia by conventional method Yadav and Nair (1999)

20 g of zirconium oxychloride (ZrOCl₂·8H₂O) was dissolved in 200 ml of deionised water in a beaker. The aqueous solution was hydrolysed with 25% ammonium hydroxide, maintained at pH 9. The resultant gel was stirred for 30 min and left for 4 h to digest before it was filtered. The resultant zirconium hydroxide was thoroughly washed with water to remove all chloride salts (this was confirmed with 0.5 N AgNO₃) and dried for 24 h at 100 °C, after which it was impregnated with 1 M H₂SO₄ (15 ml H₂SO₄ per 1 g of Zr(OH)₄) under constant stirring for 30 min. The solution was filtered and the residue was dried at 100 °C for 24 h before calcination in air at 650 °C for 3 h. It is designated as “CMSZ”.

2.2.2. Preparation of sulphated zirconia by direct method

The direct synthesis of sulphate zirconia was performed according to the methods reported in Sun et al., (2005). Zirconium oxychloride (ZrOCl₂·8H₂O) and ammonium sulphate (NH₄)₂SO₄ were carefully weighed on the basis of molar ratio 1:6 respectively into a mortar and grinding for 20 min at room temperature. The mixture was left to age for 18 h at room temperature and calcined at 600 °C for 5 h; designated as “DSSZ”.

2.3. Characterization of catalyst

The sulphated zirconias physical properties were determined using a variety of techniques. The surface areas were obtained from N₂ BET (Brunauer, Emmett and Teller) isotherms determined at 77 K using the Coulter™ (SA 3100™ series). The samples were out-gassed for 2 h at 200 °C prior to the analysis. The X-ray diffraction was performed using a Siemens D 5000 X-ray diffractometer and Cu K α radiation with a wavelength of $\lambda = 1.54 \text{ \AA}$ generated at

40 kV and 40 mA from 10 °C to 90 °C. The X-ray diffractogram, X'pert data viewer software and the Scherrer equation were used to determine the crystallite size. FTIR measurements were performed in a Varian 800 (Scimitar series) spectrometer. The spectra were produced between 4000 cm⁻¹ and 400 cm⁻¹ using a Pike Technologies diamond crystal plate ATR. Environmental Scanning Electron Microscopy was used for images and ImageJ software used to calculate the pore and particle sizes of the prepared catalysts. Elemental analysis of samples was carried out using Energy Dispersive X-ray (EDX).

2.4. Catalytic cracking of vegetable oil

67 g of rapeseed oil and 1.34 g of catalyst (2% wt of feed) was reacted in a batch reactor at 270 °C and conversion monitored against time. Samples were collected every 1 h for 4 h and all experimental conditions were repeated at least twice. The liquid fraction was analysed using Perkin Elmer (Clarus) 600/560D Gas Chromatography and Mass spectroscopy (GCMS), Hewlett Packard 5890 Series II gas Chromatography (GC).

3. Results and discussion

The main purpose of this study was to determine the effect of preparation on the catalytic activity of sulphated zirconia in thermocatalytic cracking using triglycerides. Firstly the catalysts were prepared and characterized, followed by catalytic cracking of triglycerides under different reaction conditions. The structural characteristics of the two forms of sulphated zirconia formed are clearly different. The sulphated zirconia produced by direct synthesis is amorphous, (contrasting with the findings of Sun et al. (2005)), whereas that produced by the conventional method is polycrystalline. The XRD of conventional method (CMSZ) exhibits peaks assigned to tetragonal phases of zirconia, with crystallite size of 10.42 nm whereas no crystalline phases were identifiable for directly synthesized sulphated zirconia. The IR spectra of the two forms of the catalyst, on the other hand, are similar; indicating strong, broad bands in the region 3550–3000 cm⁻¹ and weaker absorptions band at 1560–1640 cm⁻¹. Similar results were reported by Garcia et al. (2008): the strong band is due to physisorbed and coordinated water, the weaker band is assigned to the bending mode (δ HOH) of coordinated water, this agrees with the results of Sun et al., (2005). The intensity of the physically absorbed water band is a little greater for the directly synthesized sulphated zirconia. This could be due to the method of treatment of both catalysts, for instance CMSZ was preheated at 100 °C for 24 h and calcined at 650 °C whereas DSSZ was left to age at room temperature and calcined at 600 °C. Observed also is the bands between 1250 and 950 cm⁻¹ for both catalysts; typical of sulphate ions groups coordinated to the zirconium cation as reported by Sun et al. (2005) and Zhai et al. (2006). This suggests that the sulphate species in both samples are similar irrespective of the sulphating agent. However the area of this band (1250 to 950 cm⁻¹) was

Table 2
Physical properties of the both catalysts.

Catalyst type	BET surface area (m ² /g)	Pore size (μm)	Particle size (μm)	Crystallite size (nm)	Nature of phases
CMSZ	65.3	0.24	36.90	10.42	T
DSSZ	168.9	0.61	58.83	–	A

A: amorphous; T: tetragonal.

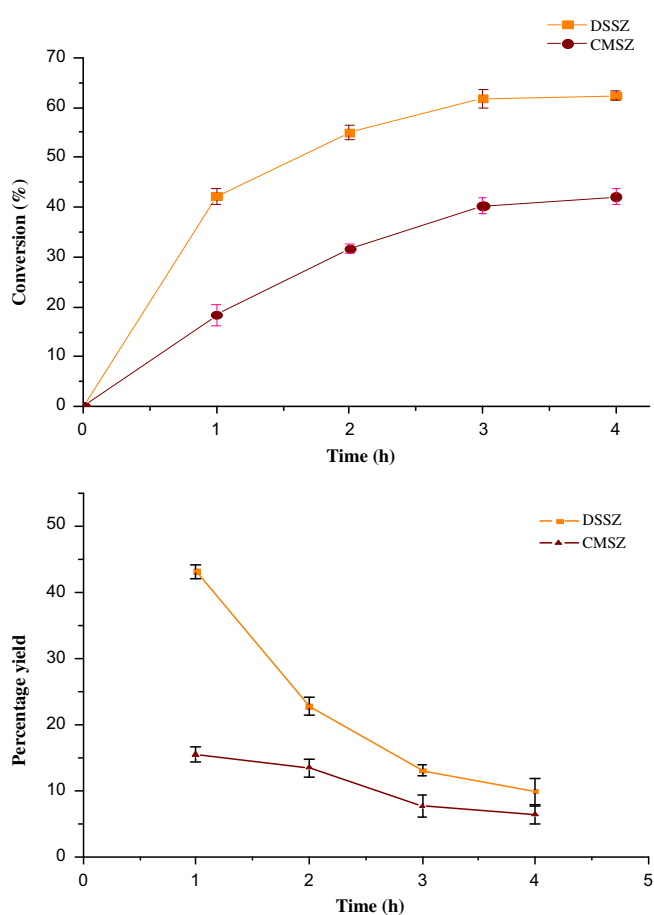


Fig. 1. Triglyceride conversion and fatty acid methyl esters yield over DSSZ and CMSZ.

larger in the case of direct synthesis, indicating the presence of more sulphate ions (about 12% higher) on the surface of the catalyst. This was further confirmed with the energy dispersive X-ray (EDX) results of the weight percentage of elements in each catalyst. DSSZ has 35:52:13 for Zr:O:S, respectively whereas CMSZ has 50:43:7. The difference in sulphate could be attributed to the preparation method.

CMSZ has a pore size 0.25 μm and particles size of 36 μm but DSSZ has 0.61 μm and 59 μm for pore and particle sizes respectively. The BET surface area was 65 m²/g and 169 m²/g for CMSZ and DSSZ, respectively (Table 2 below). The increased surface area and larger pores exhibited by DSSZ will reduce resistance to high molecular feed and, most importantly, its morphology. Amorphous substances tend to have more “defects”, and defects are often higher energy sites, therefore more catalytically active.

The infrared spectra of the adsorbed pyridine on the catalysts, confirmed the presence of Bronsted and Lewis acid sites. The bands at 1440 cm⁻¹ and 1480 cm⁻¹ correspond to Lewis acid site (Hino et al., 2006) and 1565 cm⁻¹ and 1540 cm⁻¹ are characteristic of Bronsted acid sites (Akkari et al., 2008). This is an indication of

interactions between pyridine, hydrogen ions (Bronsted site) and electrons (Lewis site) on the surface of both catalysts. However CMSZ catalyst has a relative low intensity of weak Bronsted acid sites and more of strong Lewis acid sites. The reverse is the case with the directly synthesized catalyst. With the availability of active acid sites for triglyceride molecules, primary decomposition of the triglyceride molecules and oxygen bonding of the ester carbonyl groups to heavy oxygenated hydrocarbons occurs. The decomposition of the triglyceride was also measured using FTIR. The spectra of post-reaction mixture from the DSSZ catalyst and triglyceride exhibit some profound differences/shift. The main difference is the decrease in intensity of the peaks. According to Kirszenstejn et al. (2009) this phenomenon is due to the ester bond cleavage and formation of carboxyl group. The observed bands at 740, 1470, 2850 and 2930 cm⁻¹ are characteristics of CH, CH₂ and CH₃, whereas the bands at 1750 cm⁻¹ and 1161 cm⁻¹ are ester peaks due to stretching vibration of C=O and C–O bonds, respectively. Moreover 975 cm⁻¹ is evidence of aromatics, which were not initially present in the rapeseed oil spectrum. This is due to cracking of the oxygenated compounds, and is in agreement with Dupain et al., (2007) and Melero et al. (2009).

Analysis of the liquid sample showed that directly synthesized sulphated zirconia exhibited greater activity than conventionally synthesized. The highest conversions of triglyceride observed in this work were 63% and 42% for direct synthesis and conventional method, respectively after 4 h (Fig. 1, below), with DSSZ exhibiting greater conversion. Higher sulphate concentration on the DSSZ catalyst is believed to contribute to the conversion of the feed on the catalyst. The percentage yield of methyl esters after 1 h was found to be 43% with directly synthesised catalyst and 15% for conventionally synthesised. Other products identified in the liquid sample include: monoglycerides, diglycerides, free fatty acids, alcohol and unreacted triglycerides. However the yield of fatty acid methyl esters decreased with reaction time in both cases, (Fig. 1). This could be due to deactivation of the active sites by carbon deposition on the catalysts, (1.2 g and 1.8 g of carbon after 4 h for DSSZ and CMSZ, respectively). Sulphate leaching was not significant from the IR spectra of the used and unused catalysts.

4. Conclusion

Although directly synthesised and conventionally produced sulphated zirconias both catalyse triglyceride cracking, 63% conversion of the feed was observed for the directly synthesized catalyst after 4 h, at 270 °C and greater yield for methyl ester: 43% after 1 h (decreasing afterwards). The higher surface area (169 m²/g), amorphous nature and pore size (0.61 μm) of the directly synthesized sulphated zirconia explain the higher overall activity, but the enhanced selectivity for the methyl ester and its decrease with time is the subject of further investigation, as it may be a significant process advantage of this form of the catalyst.

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