

# Effect of Modification on Conventional Preparation Method for Sulphated Zirconia on the Production of Fatty Acid Methyl Ester

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**ABSTRACT---** Sulphated zirconia was synthesized using different volume of sulphating agent in order to optimize its catalytic property: (1) in the first case the “conventional” 15 ml H<sub>2</sub>SO<sub>4</sub> to 1g of Zr(OH)<sub>4</sub> for impregnation was used in wet-precipitation method and the catalyst designated ‘wp’ and (2) same procedure but with modification in volume of acid; 2 ml of H<sub>2</sub>SO<sub>4</sub> was used for 1g of Zr(OH)<sub>4</sub>, ‘mwp’. The properties of the uncalcined and calcined catalysts were examined by various techniques: EDX, XPS, XRD, Py-DRIFTS and BET nitrogen adsorption techniques. The sulphur content in the uncalcined (‘mwp’ and ‘wp’) catalysts was the same; 0.07 mol each whereas the calcined catalysts were 0.07 mol and 0.05 mol for ‘mwp’ and ‘wp’ respectively. BET surface area was determined to be 65.0 m<sup>2</sup>/g for wp and 101m<sup>2</sup>/g for ‘mwp’. The effect of the variation of sulphating agent on the catalyst activity was investigated in catalytic cracking of triglycerides for fatty acid methyl esters. Sulphated zirconia from the modified conventional method was found to perform better than the conventional wet-precipitated sulphated zirconia. Furthermore, ‘mwp’ retained approximately 74 % of its sulphur content after 3 h reaction whereas ‘wp’ catalyst lost 100% during the reaction as indicated by SEM-EDX. Interestingly, the results show variation in characterization and in their selectivity to different types of fatty acid methyl esters under the same reaction conditions. The ‘mwp’ catalyst showed higher catalytic activity for methyl ester yield of 40 % as well as higher selectivity for saturated methyl esters

**Keywords---** Conventional method; Sulphated zirconia; Characterization; Saturated FAMES; Catalytic cracking

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## 1. INTRODUCTION

Presently transesterification of triglycerides using monohydric alcohols in the presence of homogeneous alkali catalyst is the most common process for biodiesel production. However the process is associated with a number of limitations, due to the use of homogeneous catalysts and alcohol. The most popular type of feedstock is virgin vegetable oils such as soybean oil [1] rapeseed oil, palm oil and linseed [2] However, non-edible oil [3] waste vegetable oil [4, 5] and waste animal fat could be used [6] except that this feedstock will need to undergo a pre-treatment process called esterification before they can be used successfully in transesterification. This is because of their high level of free fatty acid that could result into the formation of soap instead of the desired biodiesel. With the increased awareness of the economic and environmental implications of homogeneous catalysts, solid acid catalysts has been reported as an alternative to the homogeneous counterpart in transesterification [7] However their usage in catalytic cracking is reported to be an ideal alternative to transesterification [8] This is because it would remove the need for alcohols altogether, reducing downstream processes, and simplified flow sheet, thereby removing a substantial capital cost. In our previous work [9], it has been shown that catalytic cracking is a good process for biodiesel production. Presently, the research frontier for catalytic cracking of triglycerides is finding solid acid catalyst that is active, selective, and stable under the process conditions that could facilitate highly selective conversion of economically viable feedstocks to the desired products in the existing infrastructure. Among the many heterogeneous solid acid catalysts, zirconia doped with sulphate has attracted great attention due to their strong acid characteristics and their resulting potential as solid acid catalysts for selective hydrocarbon isomerisation and several other acid-promoted reactions [10, 11]. Thus far, sulphated zirconia has been heavily reported as super-acid catalyst with acidity [9] times stronger than 100% sulphuric acid [12, 13]. 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 [14]. Most authors reported sulphated zirconia as having more Lewis acid sites than Brønsted acid site [15]. Several authors have reported a variety of investigation on the use of sulphated zirconia in transesterification using feedstock with variety of free fatty acid [16]. However, few research studies are reported on the use of sulphated zirconia in catalytic cracking of triglycerides. Nevertheless, its commercial implementation still need more research in terms of increased stability of acid sites to avoid leaching, thermal stability, enhancement of mass transfer to avoiding diffusional limitations.

The catalytic properties of sulphated zirconia have been shown by several authors as string function of its preparation method [17-19]. An acid catalyst should be designed to exhibit combined activity and selectivity to have a positive impact on the biodiesel synthesis or any chemical reaction. Therefore, its preparation has drawn much attention among researchers; sulphated zirconias have been synthesized through different routes and conditions in order to improve its catalytic performance. It is well known that an acid solid catalyst should have moderate to high concentration of strong acid sites available for reactants to proceed to products. The conventional way of preparing sulphated zirconia has been reported to produce sulphated zirconia with small surface area and low activity [19]. Hence in the present work the volume of acid used for sulphation was modified and for comparison purpose, the conventional 15 ml H<sub>2</sub>SO<sub>4</sub> to 1g of Zr(OH)<sub>4</sub> was also prepared and their catalytic properties were investigated. Both were characterized for sulphur content, surface area, chemical state, phase composition and crystallinity.

## 2. EXPERIMENTAL

### 2.1. Catalysts synthesis

In the first instance, sulphated zirconia was prepared by conventional wet-precipitation method as described by Yadav and Nair [19]; using zirconium oxychloride octahydrate (99.5%, Sigma-Aldrich) as a precursor. A solution was prepared by mixing zirconium oxychloride (20 g) in 200 ml of distilled water. Then, ammonium hydroxide (25%) was added drop wise to the mixture and maintained at a pH 9, under constant stirring for 4 h. When the reaction was completed, the solution was filtered and thoroughly washed to remove chloride ion from the zirconium oxide. The presence of chloride ion was determined with AgNO<sub>3</sub> test. The oxide was dried by evaporation in an oven for 24 h at 100°C after which it was impregnated with 1 M H<sub>2</sub>SO<sub>4</sub> (97.5%, Sigma-Aldrich) under constant stirring for 2 h. The mixture was filtered and the resulting gel was further dried in the oven at 100°C for 24 h and finally calcined in air at 650°C for 3h to produce sulphated zirconia, denoted as 'wp' (wet-precipitated sulphated zirconia). In the case of the modified form, the sample was synthesized using same procedure, but different volume of acid was used for impregnation, 2 ml instead of 15 ml and it is designated 'mwp' (modified wet-precipitated sulphated zirconia). For the sake of comparison both calcined and uncalcined catalysts were subjected to characterization using surface techniques, and their catalytic activities were tested using triglycerides oil in a batch reactor at 270°C.

### 2.2 Sample characterization

The X-ray diffraction pattern was performed using a Panalytical X'Pert Pro Multipurpose Diffractometer (MPD) fitted with an X'Celerator and a secondary monochromator to determine the nature of the sample before and after calcination. The diffractograms were recorded from using Cu K $\alpha$  radiation with a wavelength of  $\lambda = 1.54 \text{ \AA}$  generated at 40 kV and 40 mA from 2°C to 100°C. Their crystallites size was determined using X'pert data viewer software on X-ray diffractogram to generate the necessary data that were applied in Scherrer equation. The surface area measurements were obtained from N<sub>2</sub> adsorption/desorption isotherms determined at 77K using the Coulter™ (SA 3100™ series) by applying the BET equation[20]. The samples were outgassed for 2 h at 200°C prior to the analysis. Thermal analysis was performed on both calcined and non-calcined samples in order to obtain information on the loss of sulphur resulting from the calcination process. The TG analysis was conducted on a Perkin-Elmer (Pyris STA 6000 Model) instrument. The sample was placed on a platinum crucible and heated at the rate of 5°C/min in helium stream of 30 ml/min at STP. Spectra were recorded from 30°C to 900°C and the amount of sulphate before and after calcination was determined. IR spectra of samples were performed in a Varian 800 (Scimitar series) spectrometer. The spectra were produced between 4000cm<sup>-1</sup> and 400cm<sup>-1</sup> using a Pike Technologies diamond crystal plate ATR. The XPS spectra were performed using CasaXPS 2.3.15 software on Kratos analytical system, equipped with a monochromator AlK $\alpha_{1,2}$  X-ray sources of 1486.6 eV and 0.85 eV widths. The reference used was by setting the CHx peak maximum in the resolved C 1s spectra to binding energies of 284.6 eV. Elemental analysis was investigated using energy dispersive X-ray (EDX). The nature and strength of the acids site on the catalysts was determined using Diffuse Reflectance. Infrared Fourier Transform Spectroscopy (Pyridine- DRIFTS) after pyridine adsorption and desorption. The measurements were carried out using self-supported wafer; a dilution of 5% KBr was used to avoid absorption saturation at low wave numbers and an IR spectrum was recorded after each stage.

### 2.3 Catalytic tests

Both catalysts were tested in a batch reactor (Model: 4560) equipped with a magnetic stirrer and an external heating mantle. The feed, rapeseed oil was heated from ambient room temperature to 270°C before injecting the catalyst. The

operating conditions were controlled by WinISO software and conversion monitored against time. The amount of catalyst used was 2 % weight of the feed. Sampling was performed at every 15 minutes for a reaction time of 3 h. The FAME(s) determination and quantification was according to BS EN 14103:2003. This was performed on Hewlett Packard 5890 Series II gas chromatograph with an FID detector. The column temperature was maintained at 210°C while the FID and injector were operated at 250°C each. Detailed composition of the liquid product was carried out using Perkin Elmer GCMS (Clarus) 600/560D equipped with a capillary column (15m×0.25mm, i.d. 0.25 µm film thickness), and helium as the carrier gas in order to determine the glycerides present according to BS EN 14105: 2003.

### 3. RESULTS AND DISCUSSION

The XRD measurement revealed the phase composition of the two sulphated zirconias ('mwp' and 'wp') as crystalline; the wet-precipitated sulphated zirconia ('wp') was tetragonal in nature, interestingly, the modified wet-precipitated sulphated zirconia ('mwp') exhibited not only the characteristic peaks of tetragonal phase but in addition, monoclinic ZrO<sub>2</sub> phase was observed as shown in Figure 1. Interestingly, the XRDP diffractograms of uncalcined 'mwp' and 'wp' catalysts were amorphous. This shows the effect of calcinations temperature on the catalysts as earlier observed [21]. Interestingly also, during the preparation of the modified catalyst, 2 ml of sulphuric acid was used for 1 g of ZrOH compared to the wet-precipitated catalyst where 15 ml to 1g of ZrOH was used. The appearance of the monoclinic phase in 'mwp' which is absent in 'wp' is obviously an important observation and is due to the difference in the volume of sulphate used during the preparation. This was also reported by Farcas et al [21]. Their crystallite size was 17.51 nm and 10.42 nm for 'mwp' and 'wp' respectively.

These distinct structural differences are indication that excess sulphate affects the textural properties and may not be necessary for the preparation of an active catalyst. The IR spectra of the catalysts exhibited strong absorption of sulphate ions coordinated to the zirconium cation between 1297 cm<sup>-1</sup> and 896 cm<sup>-1</sup> region. The frequencies from both catalysts were similar, suggesting that the sulphur species in both samples are similar; however, the intensity of absorption for 'mwp' catalyst is higher than the 'wp' catalyst (about 3% more). It is an indication that more sulphate ion was retained on the surface of the 'mwp' and homogeneity was achieved. The elemental analysis (EDX) and X-ray photoelectron spectroscopy (XPS) reveal similar results of higher retention of sulphur on the 'mwp' catalyst (13 wt %); almost double the weight percentage found on the 'wp' catalyst. The XPS spectra of O 1s of 'mwp' revealed a 1:1 ratio of sulphate and oxide at 532.4 eV and 530.4 eV respectively. This indicates 50% each of oxide oxygen and sulphate oxygen, whereas 'wp' had 42 % sulphate oxygen and 58 % of oxide oxygen as shown in Figure 2. The EDX also indicate equal amount of 0.07 mol sulphur content in both uncalcined catalysts ('mwp' and 'wp'), whereas the calcined catalysts had different amount of sulphur; 'mwp' had 0.07 mol and 0.05 mol for 'wp'.

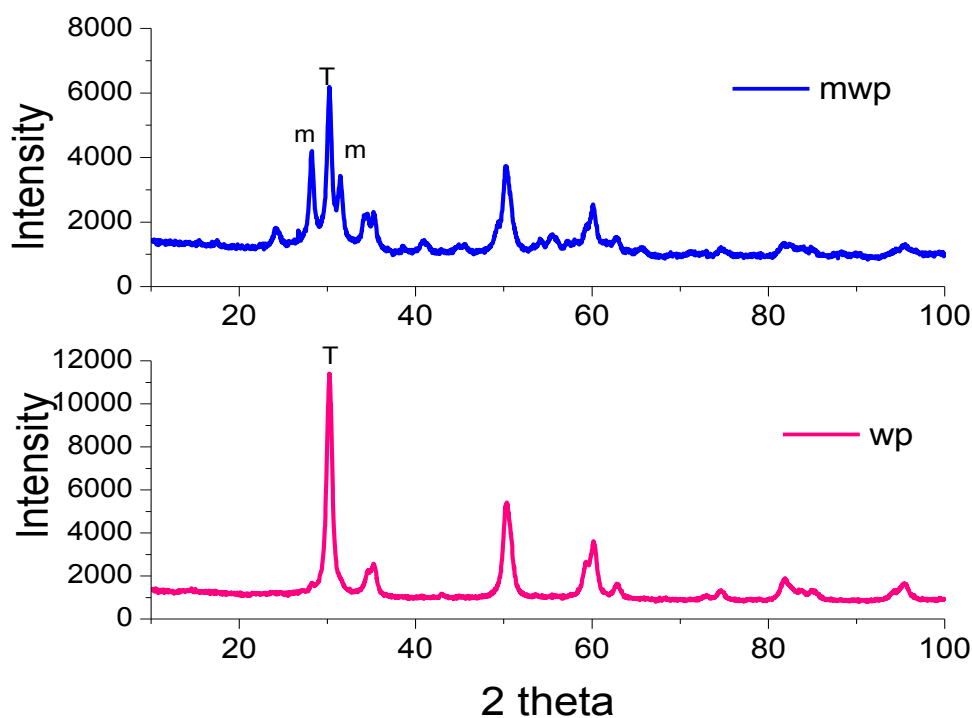


Figure 1 XRD showing the phases of the 'mwp' and 'wp' catalysts

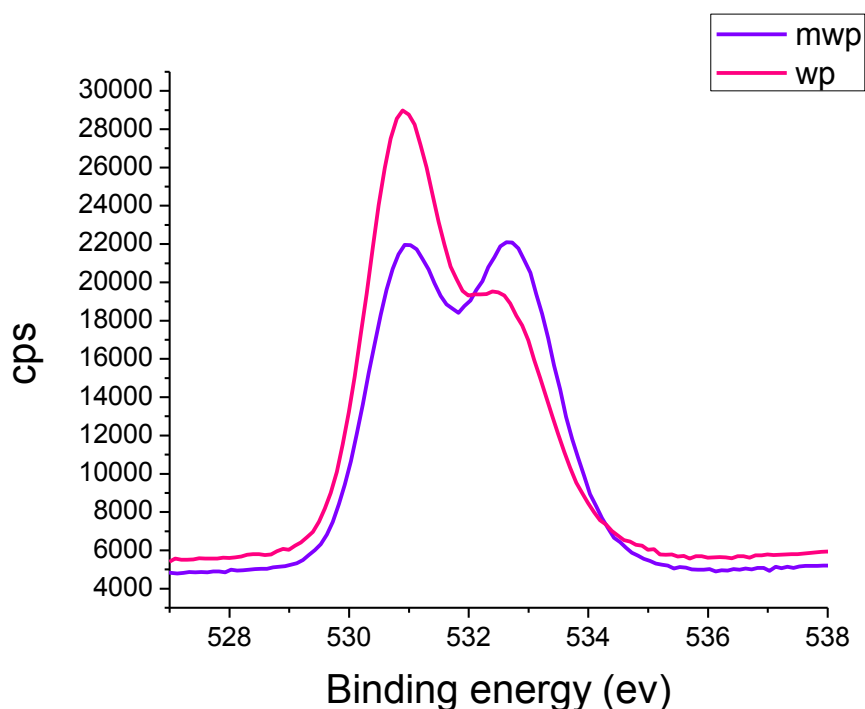


Figure 2 XPS spectra of O 1s of ‘mwp’ and ‘wp’ catalysts

From Figure 2, it is seen that the peak at 532.4 eV showing the sulphate oxygen in ‘wp’ catalyst is reduced compared to ‘mwp’. This is an indication of approximately 11% of more  $Zr(SO_4)_2$  on the surface of ‘mwp’ catalyst. This feature exhibited in ‘mwp’ is an important observation that has not been reported in any literature to the best of our knowledge. However the S 2p spectra are similar with each other and showed that the sulphate species are  $S^{6+}$  of  $SO_4^{2-}$ . The infrared spectra of the adsorbed pyridine on both catalysts, revealed bands characteristics of Brönsted and Lewis acid sites at  $1540\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$  respectively. However, the ‘wp’ has more Lewis acid site as revealed on the catalyst; (75%) and less of Brönsted acid sites (25%). The reverse is the case with the ‘mwp’ catalyst, approximately 54% of Brönsted acidity was observed, despite less amount and same source of acid that was used for impregnation of ‘mwp’ catalyst coupled with the fact that the same method of preparation was adopted.

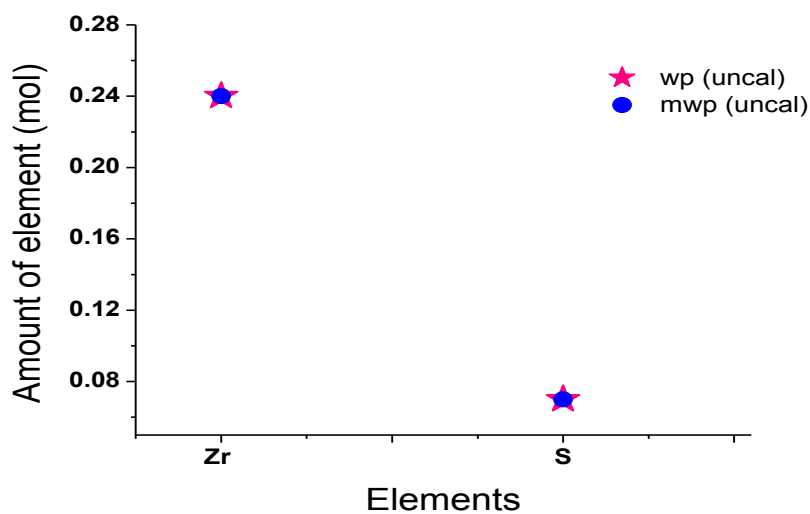


Figure 3 EDX results of sulphur in mole before calcinations of the catalysts: ‘wp(uncal)’ and ‘mwp(uncal)’ are uncalcined wp and mwp;

This is an interesting result; the ‘mwp’ not only has Brönsted acid sites but about 8% more than its counterpart, Lewis acid site. We also observed that despite the large difference in the amount of sulphuric acid used during preparation; approximately 1:8 for ‘wp’ and ‘mwp’ respectively, the same mole of sulphur was retained on the surface of the gel before calcinations (Figure 3); interestingly, the ‘mwp’ retained its sulphur content after calcination, but ‘wp’ lost 29% (Figure 4). Apparently, there was no reduction in sulphate during the post-treatment (i. e. calcination) of the ‘mwp’. This goes further to confirm the uniqueness of the modified method of preparation.

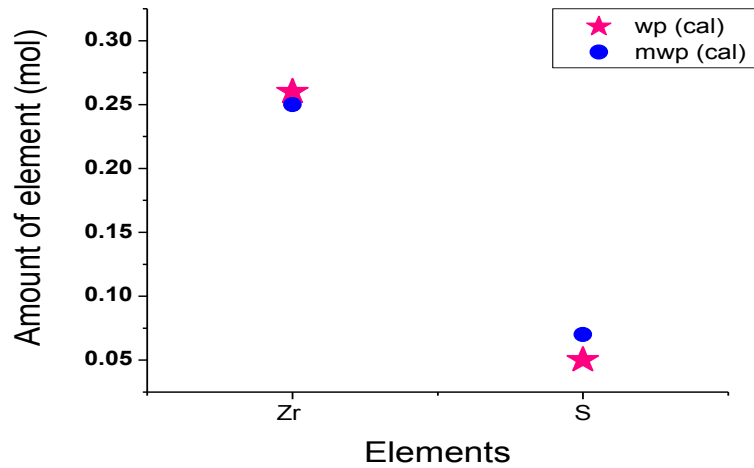


Figure 4 EDX results of sulphur in mole after calcinations of the catalysts: ‘wp(cal)’ and ‘mwp(cal)’ are calcined wp and mwp

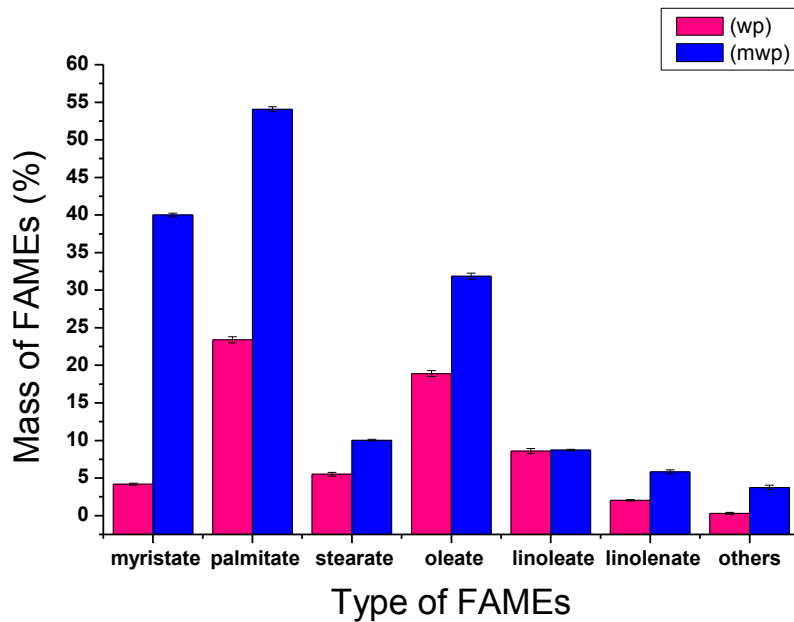


Figure 5 FAMES profile showing saturated, mono and poly unsaturated methyl ester

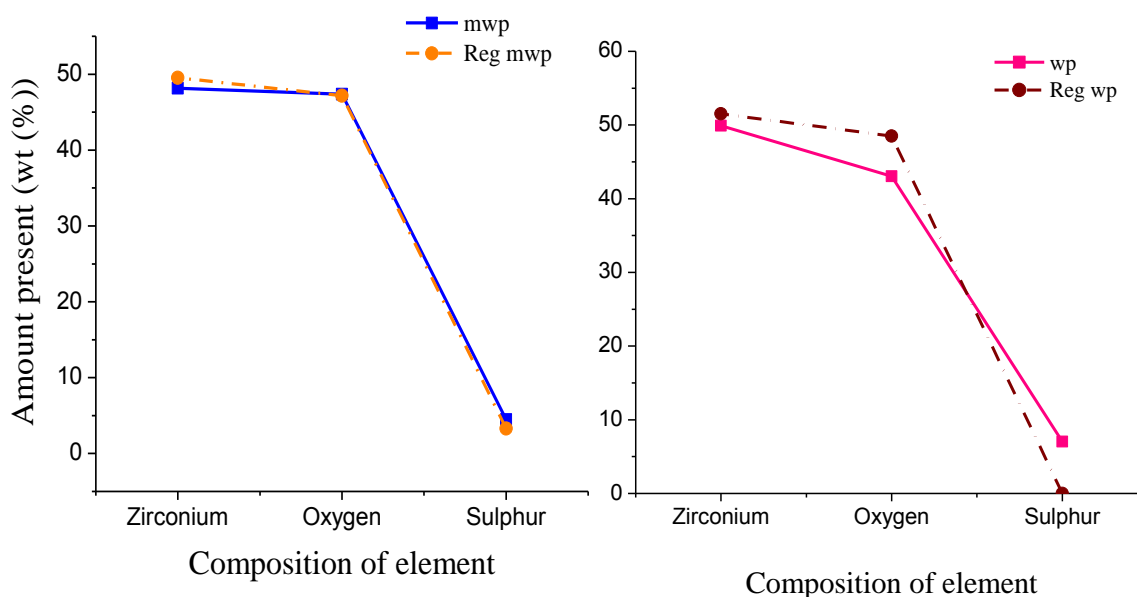


Figure 6 Comparing the retained sulphur content of both catalysts before and after used (regeneration)

The BET surface areas were  $65\text{m}^2/\text{g}$ , and  $101\text{m}^2/\text{g}$ , for ‘wp’ and ‘mwp’ respectively. The surface area and acid sites play a great role in the catalytic reactions as it is the area and amount of site available for reactions. The sulphate on the surface of the uncalcined catalysts was monitored by thermogravimetric analysis (TGA). Notably, three main mass loss regions were observed: at  $100^\circ\text{C}$  due to physisorbed water, the second between  $150 - 390^\circ\text{C}$  indicating dehydration and dehydroxylation and finally, at  $580 - 800^\circ\text{C}$  associated with sulphate decomposition. The ‘mwp’ experienced a greater sulphate loss ( $0.17\text{mol}$ ) than the ‘wp’ ( $0.11\text{mol}$ ). This no doubt confirmed the presence of more sulphate ion to zirconium cation been formed on the surface of ‘mwp’ catalyst during preparation. Both catalysts cracked triglycerides with a conversion of 58 % and 49 % after 3 h for ‘mwp’ and ‘wp’ respectively. Not only was ‘mwp’ conversions greater, it exhibited greater selectivity for total fatty acid methyl esters (FAMES), approximately 40 % after  $2\frac{1}{4}$  h and 27 % for ‘wp’ in less than 2 h. We found the fatty acid methyl esters profile was more selective for saturated methyl esters compared to unsaturated as seen in Figure 5. However, there was higher yield of the saturated methyl esters with ‘mwp’

In our case, the presence of Brönsted acid sites in both catalysts enhanced its catalytic activity and much more is the ‘mwp’ catalyst, which obviously is attributed to the reduced amount of sulphate used during preparation compared to authors [17-19] who reported sulphated zirconia catalyst as having only Lewis acid sites. Furthermore, the ‘wp’ was observed to suffer severe leaching during catalytic activity test; it lost 100% of its sulphur content after 3 h of reaction whereas ‘mwp’ lost only 26% (1.17 wt%). The weight percent of sulphur on the regenerated ‘wp’ catalyst was 0 wt%, while that of ‘mwp’ catalyst was 3.29 wt% as indicated by EDX and shown in Figure 6. This aspect of sulphate leaching needs further improvement.

#### 4. CONCLUSIONS

The variation in the volume of the sulphating agent used during preparation led to sulphated zirconias that exhibited different properties in terms of specific surface areas, acid sites, thermal stability and surface sulphate. Both catalysts were catalytically active for triglycerides cracking for fatty acid methyl esters in a catalytic reaction. The ‘mwp’ catalyst was more active with higher conversion of triglycerides and higher FAMES yield, approximately 40% after  $2\frac{1}{4}$  h, as compared to the conventionally wet-precipitation method (27%). The selectivity towards saturated esters could only be explained by the higher activity of ‘mwp’ which is as a result of the presence of higher sulphate on the surface of the catalyst as revealed by the XPS and EDX studies, as well as the increased Brönsted acid site. The activity and selectivity of both catalysts for saturated esters is an advantage and could be of interest. We can safely conclude that the conventional wet-precipitation method if modified by reducing the “conventional” volume (15 ml) of sulphating acid could be used to synthesize active sulphated zirconia catalyst with improved surface area and increased Brönsted acid site for higher catalytic activity. Importantly, we observed in this work and consequently agree with katada et al. (2000) that excess sulphating agent tends to suppress acidity. Therefore, the conventional wet-precipitation method is still viable for preparing sulphated zirconia with improved activity, structural and textural properties.

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