



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 optimise its catalytic property: (1) in the first case the "conventional" 15 ml H₂SO₄ to 1g of Zr(OH)₄ 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 H₂SO₄ was used for 1g of Zr(OH)₄, '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 m²/g for wp and 101m²/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. Interesting 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;

1. Introduction

With the increased awareness of the economical and environmental implications of homogeneous catalysts, solid acid catalysts has been reported as an alternative to the homogeneous counterpart in transesterification (Melero et al., 2009a). However their usage in catalytic cracking is reported to be an ideal alternative to transesterification, (Taufiqurrahmi and Bhatia, 2011). This is because it would remove the need for alcohols altogether, reducing downstream processes, and simplified flow sheet, thereby removing a



capital cost. Presently, the research frontier for catalytic cracking of triglycerides is to find a solid acid catalyst that is active, selective, and stable under the process conditions to 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 acidic characteristics (Ardizzone et al., 1997; Arata et al., 1990). Thus far, sulphated zirconia has been widely reported as super-acid catalyst with acidity 10⁴ times stronger than 100% sulphuric acid, (Katada et al., 2000; Hino et al., 1979). However it has been found to have a relatively low surface area and known to suffer leaching (Hino and Arata, 1994). Several authors reported sulphated zirconia as having more Lewis acid sites than Brönsted acid sites (Morterra et al., 1994). There are several reports on the use of sulphated zirconia in catalytic cracking using different feedstock (Melero et al., 2009b). However, few research reports are reported on the use of sulphated zirconia in catalytic cracking of triglycerides.

The catalytic properties of sulphated zirconia have been shown by several authors as a function of its preparation method, (Yadav and Nair, 1999; Davis et al., 1994; Yamaguchi, 1994). Therefore, its preparation has drawn much attention among researchers. Sulphated zirconia catalysts have been synthesized through different routes and conditions in order to improve their catalytic performance. The conventional way of preparing sulphated zirconia is by wet-precipitation method; this method has been reported to produce sulphated zirconia with low surface area and low activity (Yadav and Nair, 1999). Hence in the present work the conventional wet-precipitation method was modified in terms of the volume of acid used for precipitation. For comparison purpose, a conventional sulphated zirconia was also prepared. The catalysts were characterized for sulphur content, surface area, chemical state, phase composition and crystallinity. The overall aim is to study the effect of the volume of precipitating agent during sulphation on its catalyst activity in the production of fatty acid methyl esters.

Experimental

The method described by Yadav and Nair, 1999 was used in the preparation of the sulphated zirconia catalysts. In the first instance the normal 15ml of H₂SO₄ to 1g Zr(OH)₄ was used, denoted as 'wp' (wet-precipitated sulphated zirconia). In the second case the catalyst was synthesized using same procedure but different volume of acid for precipitation; 2 ml of H₂SO₄ to 1g Zr(OH)₄ and it is designated 'mwp' (modified wet-precipitated sulphated zirconia). For effective analysis both uncalcined and calcined catalysts were subjected to characterization using surface techniques, and their catalytic activities were tested using triglycerides oil in a batch reactor at 270°C. X-ray diffraction was used to determine their crystallinity. Their crystallites size was determined using X'pert data software on X-ray diffractogram to generate the necessary data that were applied in Scherrer equation. 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 surface area measurements were obtained from N₂ adsorption/desorption isotherms determined at 77K. Both catalysts were tested in a batch reactor equipped with a magnetic stirrer and an external heating mantle. The amount of catalyst used was 2 % wt 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.

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 ZrO₂ phase 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 by Farcas, iu et al. (1997). 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, iu et al. (1997). Their crystallite size was 17.51 nm and 10.42 nm for 'mwp' and 'wp' respectively.

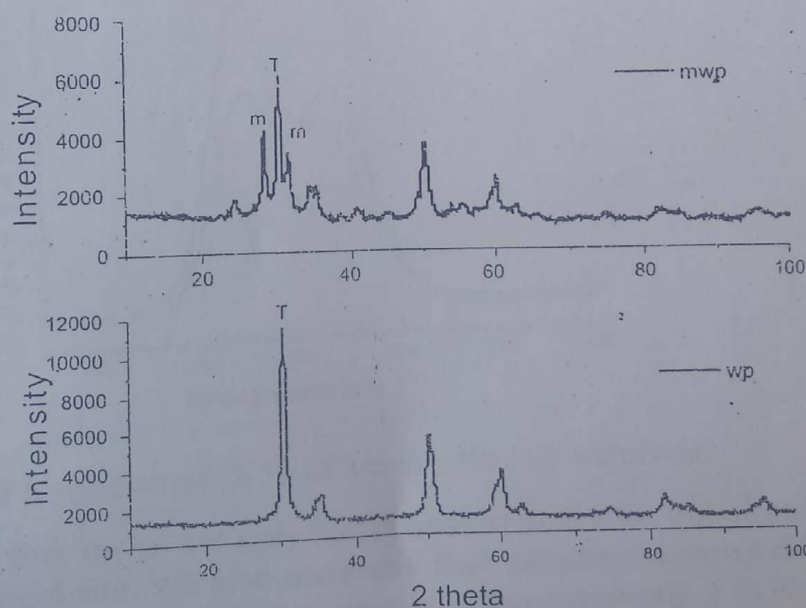


Figure 1 XRD showing the phases of the 'mwp' and 'wp' catalysts

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 (Katada et al., 2000).

The IR spectra also revealed similar sulphur species on both catalysts. However, the intensity of absorption for 'mwp' catalyst is higher than the 'wp' catalyst. This 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



...1 ratio of sulphate and oxide at 532.4 eV and 530.4 eV respectively. This indicates 50% 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 0.07 mol and 0.05 mol of sulphur; for 'mwp' for 'wp' respectively. 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-} . This is in agreement with Hino et al. (2006). The infrared spectra of the adsorbed pyridine on both catalysts, revealed bands characteristics of Brönsted and Lewis acid sites at 1540 cm^{-1} and 1450 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 lesser amount, same method and same source of acid used for impregnation.

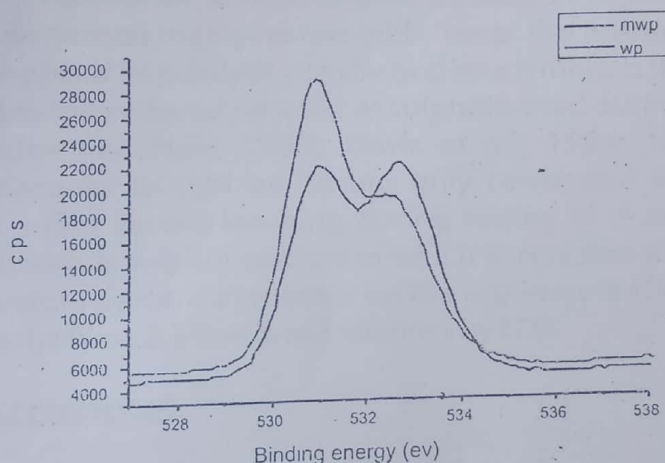


Figure 2 XPS spectra of O 1s of 'mwp' and 'wp' catalysts

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. Interestingly, the 'mwp' retained its sulphur content after calcination, but 'wp' lost 29%. Apparently, therefore, there was no reduction of sulphate during the post-treatment (i. e. calcination) of the 'mwp'. This goes further to confirm the uniqueness of the modification in preparation.

The BET surface areas were 65 m^2/g , and 101 m^2/g , for 'wp' and 'mwp' respectively. The sulphate on the surface of the uncalcined catalysts was monitored by thermogravimetric analysis (TGA). The 'mwp' experienced a greater sulphate loss (0.17 mol) than the 'wp' (0.11 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 59 % and 47 % 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 21/4 h and 27% for 'wp' in less than 2 h.

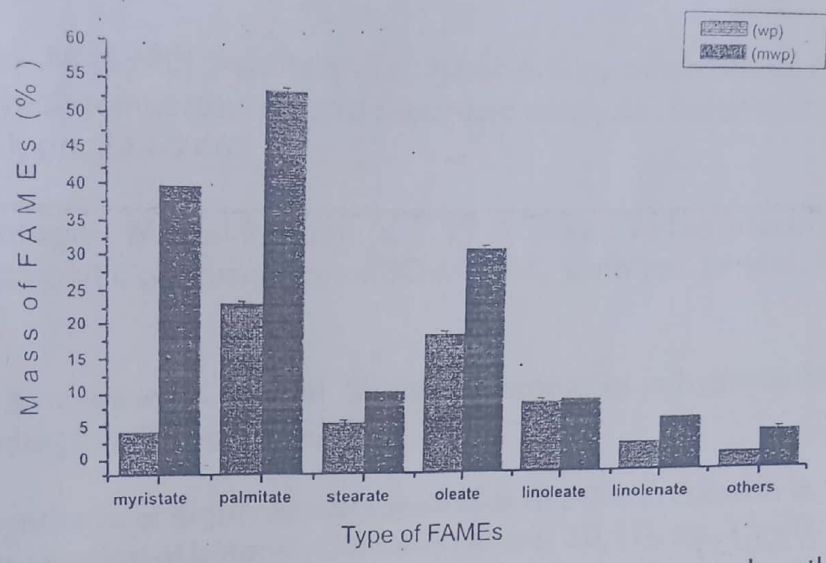


Figure 3 FAMES profile showing saturated, mono and poly unsaturated methyl ester. We found interestingly the fatty acid methyl esters profile was more selective there was higher methyl esters compared to unsaturated as seen in Figure 3. In addition there was higher yield of the saturated methyl esters with 'mwp' 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 other authors (Yadav and Nair, 1999; Davis et al., 1994; Yamaguchi, 1990) who reported sulphated zirconia catalyst as having only Lewis acid sites. Furthermore, the 'wp' was observed to suffer severe leaching during testing of their catalytic activity. Analysis show 'wp' 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

1. 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 21/4 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 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 synthesized 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



ed zirconia with improved activity, structural and textural properties

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