



Structural and Acidity Studies of Sulphated Zirconia Catalyst Prepared from Solid Sulphates by Environmental Friendly Method

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ABSTRACT

Non-crystalline sulphated zirconia catalysts were synthesised by a non-aqueous and non-conventional method. The effect of varying the ratio of sulphating agent to zirconium source was also investigated. The samples were characterized by X-ray diffraction, Energy Dispersive X-ray (EDX), Infra red Spectroscopy (IR), X-ray Photoelectron Spectroscopy (XPS). The surface acidity was measured by the Pyridine-DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) technique. The structural and textural properties of the sulphated zirconias were studied. The EDX and XPS profiles suggested that both sulphated zirconia catalysts have similar zirconia and sulphate structures; however, both catalysts were amorphous. The deconvoluted spectra of oxygen 1s confirmed the presence of oxide oxygen of zirconium and sulphate oxygen on the catalysts. Sample I had a higher amount of sulphate oxygen than sample II. Adsorption of pyridine into both samples indicated higher amounts of Brönsted acid sites in sample I, although, lower amount of sulphate was used during preparation. This opens up the possibility of controlling the degree and type of active sites on a catalyst by the amount of sulphate used for preparation.

Keywords: *Non-conventional method; Sulphated zirconia; characterization; acidity*

1. INTRODUCTION

The use of heterogeneous catalysts have gained attention and recently in the industry because of its advantages over its homogeneous counterpart. Some of the advantages include; easy recovery after reaction, good thermal stability and environmentally friendly. The main challenge is to develop a catalyst that exhibits high activity and selectivity towards the production of the desire product(s). Several routes to synthesizing solid acid catalysts have been developed (Ezekoye *et al.*, 2014). Ezekoye *et al.* (2014) reported the synthesis of various super-acid materials over the last 20 years, as well as developing procedures to produce solid super-acids of extreme acidity on several catalyst supports including metal oxides. Among the many heterogeneous solid acid catalysts, zirconium oxide doped with sulphate has attracted considerable attention for selective hydrocarbon isomerisation, esterification and various other acid-promoted reactions (Berrones *et al.*,

2014). However, Yadav and Murkute (2006) earlier noted it has a small surface area. Grecea *et al.* (2012) investigated the use of sulphated zirconia as a robust superacid catalyst for multiproduct fatty acid esterification. They observed that the preparation method of the catalyst led to considerable variation in the surface area of the catalyst and in turn the yield of their product. Jiang *et al.* (2010) amongst others specifically reported the preparation method as being pivotal to controlling the catalytic properties of catalysts. Hence, numerous methods of preparation of sulphated zirconia have been developed (Sharma and Singh, 2013) with the aim of optimising its catalytic performance in terms of acid strength and type of acidity to enhance selectivity. Taufiqurrahmi and Bhatia (2011) compared colloidal sol-gel and impregnation technique for preparation of sulphated zirconia catalyst. The catalyst from the colloidal sol-gel was found to retain more sulphates; with both Lewis and Brönsted acid sites being present (Lewis acid site was



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predominant). Early reports emphasized the importance of the crystalline phase of zirconia, sulphur species, textural properties and calcination temperature (Thomas and Thomas, 2005) on the generation of acidity of sulphated zirconia. Studies by Berrones *et al.* (2014) indicated that the crucial factor for super acidity in sulphated metal oxides is sulphur concentration instead of coordination and surface density of the sulphate. They reported that lower concentrations of sulphur (< two 'S' atoms/nm²) resulted in Lewis acidity, and higher concentration (> two 'S' atoms/nm²) in Brönsted acidity. An interesting controversy is the exact type of acid site responsible for the catalytic activity in a reaction. Muthu *et al.* (2010) claim it is only the Lewis acid sites, whereas Sharma and Singh (2013) claimed that it is only Brönsted and Eterigho *et al.* (2014) agreed both coexist. In this work, non crystalline sulphated zirconia catalysts were synthesized by non-conventional method. For the purpose of analysis of activity of the catalyst, it was compared with conventional ratio of sulphating agent to the metal oxide. The ultimate aim of this research is to develop sulphated zirconia with active sites for reactions such as isomerisation of n-butane, hydrocracking, alkylation, esterification, transesterification and thermocatalytic cracking of triglycerides.

2. METHODOLOGY

2.1. Sample Preparation

Non aqueous method was used to synthesize sulphated zirconia catalysts. This involved thorough mixing of zirconium oxychloride octahydrate (99.5%, Sigma-Aldrich) and ammonium sulphate (97.5%, Sigma-Aldrich) in ratio 1:6 and 1:15 of the reactants respectively. This was done with the aid of mortar and pestle. The mixture was left to age at room temperature for 18h to allow for homogenization before calcination at 600°C for 5h. The catalysts were designated as 'sample I and sample II' respectively.

2.2. Catalyst Characterization

The size and morphology of the samples were determined by Energy Dispersive X-ray (EDX). The surface acidity was measured by the Pyridine-DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) technique using a Thermo Avatar FTIR spectrometer. Samples were diluted to 5 wt% in KBr after which they were exposed to pyridine vapour in a vacuum desiccator at room temperature for 20 h. XPS spectra were recorded on Kratos Axis HSi analytical system, equipped with a monochromated AlK_{α1, 2} X-ray sources and charge neutraliser. Spectra were processed using CasaXPS 2.3.15 software, with energy referencing performed by setting the CH_x peak in the high resolution C 1s spectra. XRD measurements of the samples were made 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 calcination as well as phases after calcinations. The diffractograms were recorded using Cu K_α radiation with a wavelength of $\lambda = 1.54\text{Å}$. The BET surface areas were measured using the isothermal adsorption/desorption N₂ at 77K using the Coulter™ SA 3100™ series. The samples were outgassed for 2h at 200°C prior to the analysis. The numbers of Brönsted and Lewis acid sites were calculated using Equation 1 (Rattanaphra *et al.*, 2010):

$$N_T = \frac{A_L \times C_d}{\epsilon_L m} + \frac{A_B \times C_d}{\epsilon_B m} \quad (1)$$

where:

N_T is the total number of pyridine/g of sample adsorbed (μmol)

A_L/A_B is the integrated absorbance (cm^{-1}) at Lewis (L) or Brönsted (B) sites

C_d is the cross sectional area (cm^2) of the pressed disk

m is the mass (g) of the pressed disk, and

ϵ_L/ϵ_B is the molar absorption coefficient for pyridine at Lewis (L) or Brönsted (B) sites ($\text{cm}^2\text{mol}^{-1}$).

3. RESULTS AND DISCUSSIONS

3.1. Catalyst Characterization

The BET surface area and elemental analysis (EDX) of the synthesized catalysts are given in Table 1. Samples were generally found to have better structural properties compared to those reported by other authors (Sun *et al.*, 2008; Sharma and Singh, 2013; Ezekoye *et al.*, 2014). A notable achievement is the BET surface area and the ratio of sulphate oxygen to that of oxide oxygen as shown in Table 1.

Table 1: Textural properties and elemental analysis of the synthesized catalysts

Catalyst	BET (m^2/g)	O ₂ of SO ₄ ²⁻ / O ₂ of Zr (from O1s in XPS)	Crystallite size (nm)	Elemental analysis (wt%)		
				Zr	O	S
Sample I	168	10.5	A	35.5	51.6	12.9
Sample II	102	3.2	A	42.1	49.2	8.7

A= amorphous

3.1.1 XRD Analysis

The diffractogram patterns of the two prepared sulphated zirconia catalysts by non-aqueous method, designated as sample I and sample II respectively are presented in Figure 1. Both samples were amorphous irrespective of the amount of sulphate used during preparation of the catalyst. The amorphous state of the catalysts is in agreement with Sun *et al.* (2008).

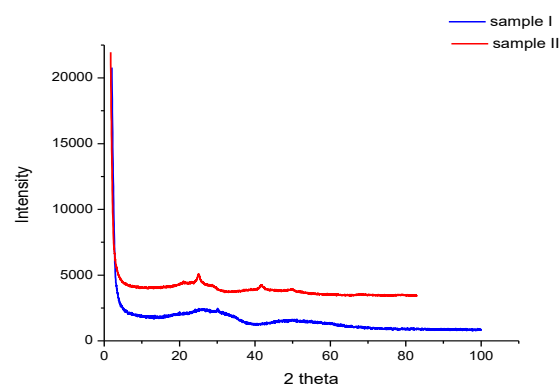


Fig. 1: Diffractogram Patterns of the Samples

3.1.2 FT-IR in the Presence of a Probe Molecule

The sulphate on the catalysts was initially determined by FTIR without pyridine. The spectra are similar as shown in Figure 2; showing strong, broad bands in the region 3550–3000 cm^{-1} due to physisorbed and coordinated water followed by weaker absorption at 1560-1640 cm^{-1} assigned to the bending mode (δHOH) of coordinated water (Sun *et al.*, 2008). The bands at 1300 to 950 cm^{-1} for the catalysts are typical of sulphate ions coordinated to the zirconium cation (Ezekoye *et al.*, 2014). However, the intensities of these bands differ with respect to the amount of sulphate used for catalyst preparation. The spectra indicated more sulphate on sample I.

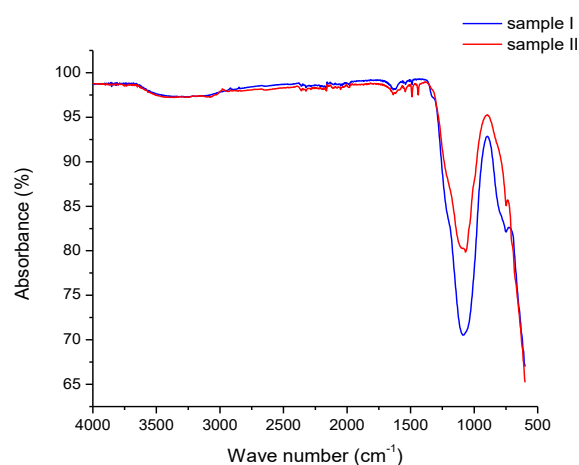


Fig. 2: IR Spectra of the Catalysts

However, this technique could not distinguish between types of acid site. This was instead achieved by DRIFT-pyridine measurements, which indicated different sites according to the sulphur content (Figure 3). The spectra in Figure 3 are a typical pyridine-IR absorption bands for sulphated metal oxides (ASTM D-4824-88). Samples show IR absorption bands between $1475 - 1500\text{cm}^{-1}$, which are assigned to adsorbed pyridine forming Lewis-type adducts. Also a well-defined adsorption bands around $1510-1563\text{cm}^{-1}$ due to Brönsted acid sites.

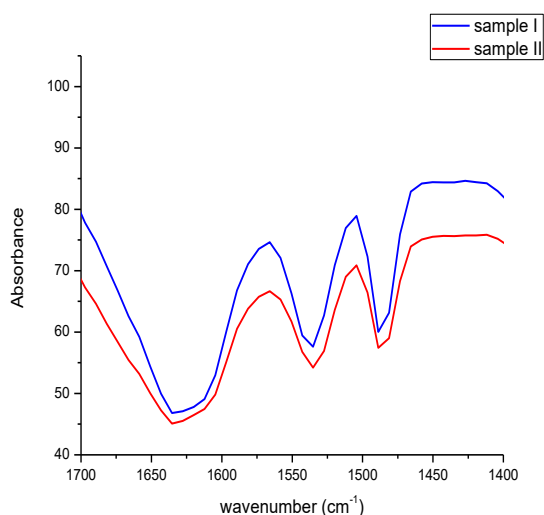


Fig. 3: FT-IR Spectra of Adsorbed Pyridine showing both Lewis and Brönsted sites

The absorbance of these bands varies. The intensity of the band between $1510-1563\text{cm}^{-1}$ assigned to adsorbed pyridine on Brönsted acid site on sample I is 21%, while the intensity on sample II is 12%. Generally, sample II exhibited reduced band intensities of both acid types. This implies sample I was able to retain more sulphate on the surface that interacted with the probe molecules. The percentages of acid sites that were Brönsted and Lewis were estimated using the relative integrated area of the pyridine species adsorbed on the sites (Grecea *et al.*, 2012). It was observed that, despite the higher amount of sulphate being used for

samples II, it experienced a substantial reduction in the percentage area of sites that were Brönsted acidic. Using Equation 1 the different amount of Brönsted and Lewis acid sites on the catalysts was evaluated.

3.1.3 X-ray Photoelectron Spectroscopy (XPS)

The XPS data were compared with the standard from Moulder *et al.* (1995). The binding energies as shown in Figure 4, correspond to zirconium in oxidation state of IV and the same binding energy was recorded for both Zr $3d^5$ and $3d^3$ in both samples.

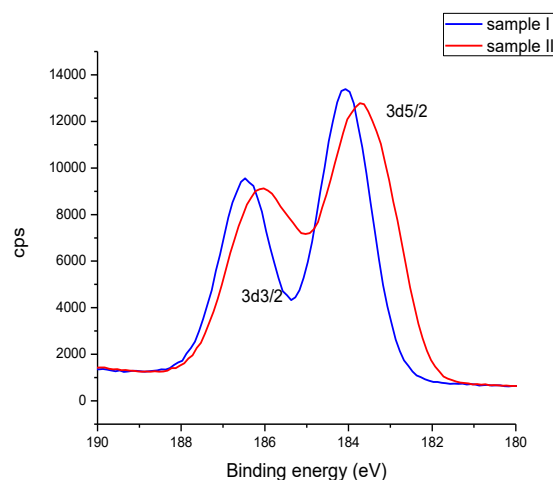


Figure 4: XPS Zr 3d Spectra of the Catalysts

The binding energies of Zr $3d^5$ and $3d^3$ were at 183.1eV and 185.5eV, respectively. However, the binding energy between the doublets was found to be the same (2.4eV) irrespective of the amount of sulphate during preparation. All samples showed same acidic zirconium species. From this data, the amount of sulphate during preparation seems to have no effect on the XPS Zr state. The binding energies of sulphur were recorded in the region of 2p energies, as presented in Figure 5, which exhibits a pronounced asymmetry.

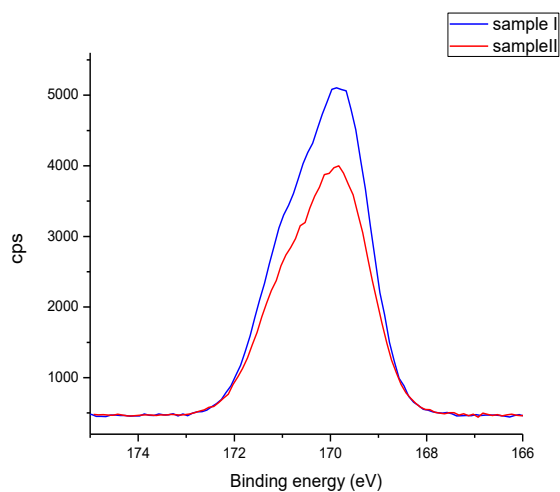


Fig. 5: XPS S 2p Spectra of the Catalysts

Deconvolution of these peaks led to two components, one located around 169.5eV and another between 170/171eV which are attributed to the S 2p_{1/2} and 2p_{3/2}, respectively. These binding energies correspond to sulphur in sulphate; in agreement with other authors (Ezekoye *et al.*, 2014; Grecea *et al.*, 2012). Clearly, the O1s spectra for both samples were consistent as shown in Figure 6, indicating the presence of S⁶⁺ in SO₄²⁻. Oxide oxygen of the zirconia at binding energies of 530.5eV/531.0eV and 532.5eV assigned to sulphate oxygen on the surface of the catalyst (Moulder *et al.*, 1995) were observed.

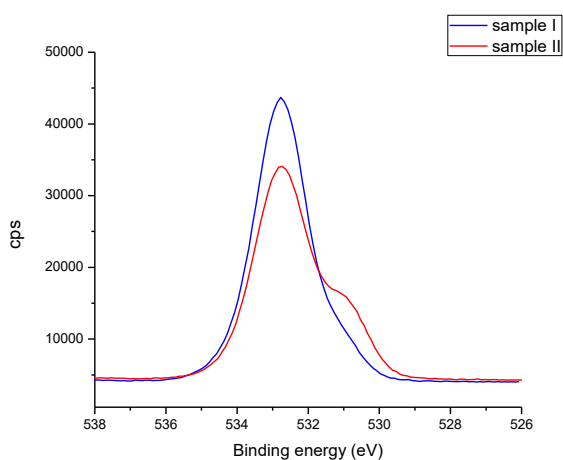


Fig. 6: XPS O 1s Spectra of the Catalysts

The peak at 530.5eV/531.0eV is higher for sample II indicating higher oxide oxygen. However, sample I exhibited higher peaks at binding energy 532.5eV as shown in Figure 7, corresponding to sulphate oxygen which resulted into its higher Brönsted acid site.

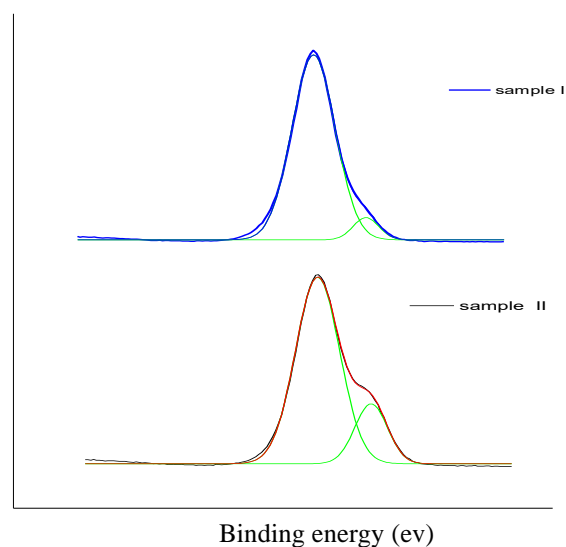


Fig. 7: Deconvoluted O 1s Spectra of the Catalysts

Surprisingly sample I, though prepared with a smaller amount of sulphating agent has its ratio of oxide oxygen and sulphate oxygen to be 10.5, whereas sample II has 3.2 in favour of oxide oxygen. This unique observation is assumed to be due to the controlled ratio of zirconium oxychloride octahydrate to ammonium sulphate used in the preparation, which results in a remarkable level of Brönsted acidity from the IR-pyridine analysis on sample I. Although excess sulphate was used in sample II, yet it retained less. One could conclude that the amount of sulphate used for sample II was greater than the threshold value as reported by Berrones *et al.* (2014), hence the lower retention of sulphate on the catalyst. The authors reported that at higher sulphate loading the sulphate moves into the bulk phase of the catalyst rather than on the surface. These distinct differences are indications that excess sulphate may not be necessary for the preparation of an active catalyst.



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4. CONCLUSION

Comparing the structural and textural properties of the sulphated zirconias by non-aqueous method in this study with the conventional method as reported by other researchers (Grecea *et al.*, 2012; Berrones *et al.*, 2014) suggest that the non-aqueous method and sulphate source facilitate a better interaction between sulphate groups and zirconia cations. In both samples it is evident that there is a direct relationship between the number of Brönsted acid sites and the amount of sulphate retained on the catalysts: this is in good agreement with Rattanaphra *et al.* (2010). The non-aqueous preparation method resulted into amorphous, Brönsted-dominated catalysts. Increasing the amount of sulphate to improve the structural and textural properties was counterproductive, as it actually decreased the physicochemical properties responsible for activity. In this study it is also shown that the tetragonal phase of sulphated zirconia is not necessarily required for Brönsted acid site formation. Also, that sulphated zirconia catalyst with higher activity properties can be achieved via a non-aqueous and environmentally friendly method.

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