



## Sulphated Zirconia Catalyst Prepared from Solid Sulphates by Non-aqueous Method

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### A B S T R A C T

Non-crystalline sulphated zirconia catalysts were synthesised by a non-aqueous and non-conventional method. The effect of varying the molar 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 zirconia were studied. The EDX and XPS profiles suggested that both sulphated zirconia catalysts have similar zirconia and sulphate structures; however, both catalysts were amorphous. Deconvolution of their XPS O 1s spectra showed that the samples contained both oxide oxygen of zirconium and sulphate oxygen, which sample I showed a higher amount of sulphate oxygen. Adsorption of pyridine into the samples indicated that the higher amounts of Brønsted acid sites are presented in sample I with lower amount of sulphate 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. Sulphated zirconia catalyst with higher activity properties was achieved via a non-aqueous, environmental friendly method. The zirconia catalyst has great contribution towards energy production which is used for preparation and transesterification of fatty acids for production of biodiesel.

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### INTRODUCTION

Heterogeneous catalysts have gained special attention in research and recently in the industry because of the 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 exhibit high activity and selectivity towards the production of the desired product(s). Several routes to synthesize solid acid catalysts have been developed. [1] reported the synthesis of various super-acid materials over the past 20 years, as well as developing procedures to produce solid super-acids of extreme acidity on several catalyst supports including metal oxides. Researchers investigated the use of alumina and a modified form of catalyst with boron oxide. They observed that the preparation method of the modified catalyst led to considerable variation in the surface area of the catalyst and in turn the yield of their product. Among the number of heterogeneous solid acid catalysts, zirconium oxide doped with sulphate has

attracted considerable attention for selective hydrocarbon isomerisation and various other acid-promoted reactions. However, it has a small surface area [2]. The authors [3][3] amongst others specifically reported the preparation method as being pivotal to control the catalytic properties of sulphated zirconia. Hence, numerous methods of preparation of sulphated zirconia have been developed with the aim of optimising its catalytic performance in terms of acid strength and type of acidity to enhance selectivity. Some authors 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 Brønsted acid sites being present (although Lewis acid site was predominant). Although early reports emphasized the importance of the crystalline phase of zirconia, sulphur species, textural properties and calcination temperature [4, 5] on the generation of acidity of sulphated zirconia. Later studies by [6] indicated that the crucial factor for superacidity in sulphated metal oxides is instead the coordination and surface density of the sulphate. They reported that lower

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concentrations of sulphur (< two 'S' atoms/nm<sup>2</sup>) resulted in Lewis acidity, and higher concentration (> two 'S' atoms/nm<sup>2</sup>) in Brönsted acidity. An interesting controversy is the exact type of acid site responsible for the catalytic activity in a reaction. [6] claimed it is only the Lewis acid sites, whereas [7] claim that it is only Brönsted and [8] agreed both coexist. In this work, non-crystalline sulphated zirconia catalysts were synthesized by non-conventional method, varying the molar ratio of sulphating agent to the metal oxide. The ultimate aim of this research was to develop sulphated zirconia with active sites for reactions.

## MATERIAL AND METHODS

### Sample preparation

Two catalyst samples were prepared (samples I and II) via the "non-aqueous" method. This involved thorough mixing of zirconium oxychloride octahydrate (99.5%, Sigma-Aldrich) and ammonium sulphate (97.5%, Sigma-Aldrich). This was done with the aid of mortar and pestle. The mixture was left to age at room temperature for 18h before calcination at 600°C for 5h. In preparing sample I a molar ratio of 1:6 of zirconium oxychloride octahydrate to ammonium sulphate was used, while sample II was prepared using 1:15 of zirconium oxychloride octahydrate to ammonium sulphate, respectively.

### 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 $\alpha$ 1, 2 X-ray sources and charge neutraliser. Spectra were processed using CasaXPS 2.3.15 software, with energy referencing performed by setting the CH<sub>x</sub> peak in the high resolution C 1s spectra to a binding energy of 284.6eV. 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 $\alpha$  radiation with a wavelength of  $\lambda = 1.54 \text{ \AA}$  generated at 40 kV and 40mA from 2 $\theta$ C to 100 $\theta$ C. The BET surface areas were measured using the isothermal adsorption/desorption N<sub>2</sub> at 77K using the Coulter TM SA 3100 TM series. The samples were out gassed for 2h at 200°C prior to the analysis. The numbers of Brönsted and Lewis acid sites were calculated using the equation below.

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

where:

NT is the total number of pyridine/g of sample adsorbed ( $\mu\text{mol}$ )

AL/AB is the integrated absorbance (cm<sup>-1</sup>) at Lewis (L) or Brönsted (B) sites

C<sub>d</sub> is the cross-sectional area (cm<sup>2</sup>) of the pressed disk

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

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

## RESULTS AND DISCUSSION

### 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. A notable achievement is the BET surface area and the ratio of sulphate oxygen to that of oxide oxygen as shown in Table 1.

### XRD analysis

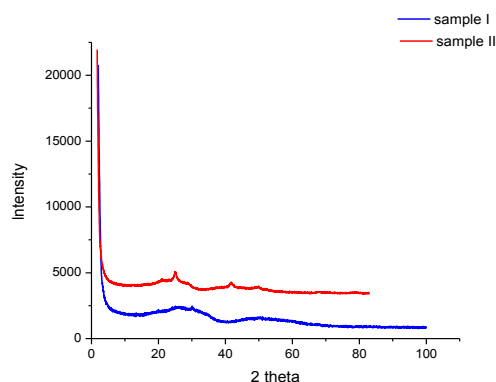
The diffractogram patterns of the two-prepared sulphated zirconia by non-aqueous method, designated as samples I

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

Catalyst	BET (m <sup>2</sup> /g)	O <sub>2</sub> of SO <sub>4</sub> <sup>2-</sup> / O <sub>2</sub> 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

and II, respectively are presented in Figure 1. Both samples were amorphous irrespective of the amount of sulphate used during preparation of the catalyst.



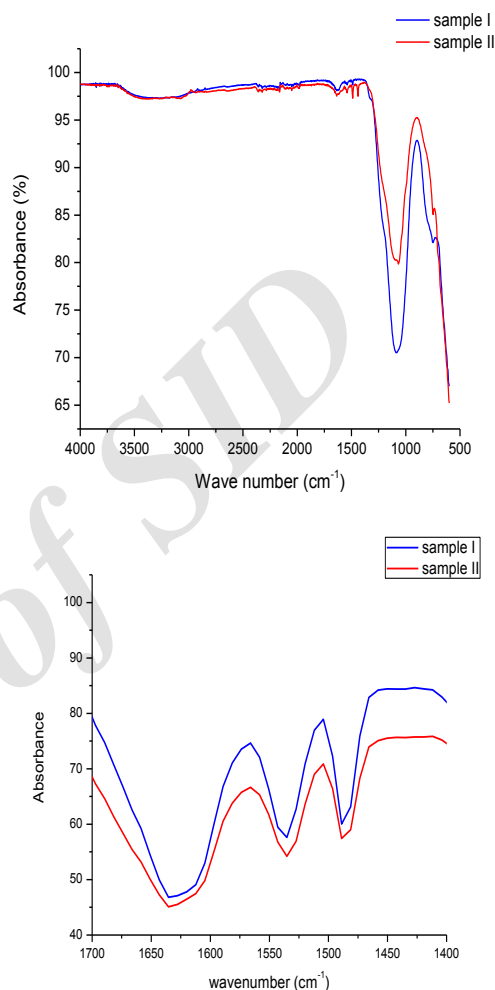
**Figure 1:** Diffractogram Patterns of the Samples. 3.1.2 FT-IR Study in the Presence of a Probe Molecule

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  $3550\text{--}3000\text{cm}^{-1}$  due to physisorbed and coordinated water followed by weaker absorption at  $1560\text{--}1640\text{cm}^{-1}$  assigned to the bending mode ( $\delta\text{HOH}$ ) of coordinated water. The band at  $1300$  to  $950\text{cm}^{-1}$  for the catalysts are typical of sulphate ions coordinated to the zirconium cation [9]. 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. 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). Pyridine on the Catalysts showing both

#### Lewis and Brönstead sites on the catalysts

The spectra in Figure 3 are a typical pyridine-IR absorption bands for sulphated metal oxides [6]. Samples showed IR absorption bands between  $1475\text{--}1500\text{cm}^{-1}$ , which are assigned to adsorbed pyridine forming Lewis-type adducts. Also, a well-defined adsorption bands around  $1510\text{--}1563\text{cm}^{-1}$  due to Brönsted acid sites. The absorbance of these bands varies. The intensity of the band between  $1510\text{--}1563\text{cm}^{-1}$  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. 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.



**Figure 2:** IR Spectra of the Catalysts. Figure 3: FT-IR Spectra of Adsorbed

#### X-ray Photoelectron Spectroscopy (XPS)

The XPS data were compared with the standard from [10]. 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 samples I and II.

The binding energies of Zr  $3d^5$  and  $3d^3$  were at  $183.1\text{eV}$  and  $185.5\text{eV}$ , respectively. However, the binding energy between the doublets was found to be the same ( $2.4\text{eV}$ ) irrespective of the amount of sulphate during preparation. All samples showed same acidic zirconium species. From this data, the amount of sulphate during preparation

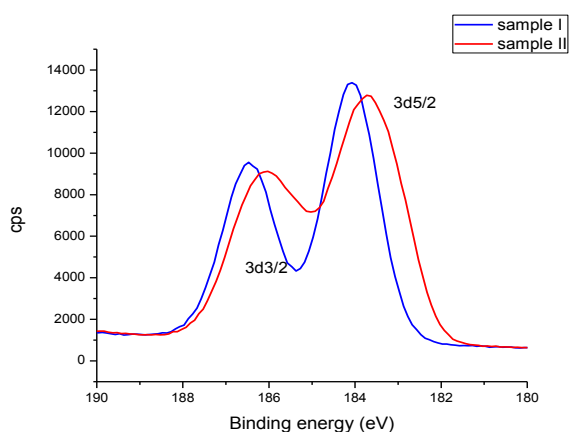


Figure 4. XPS Zr 3d Spectra of the Catalysts

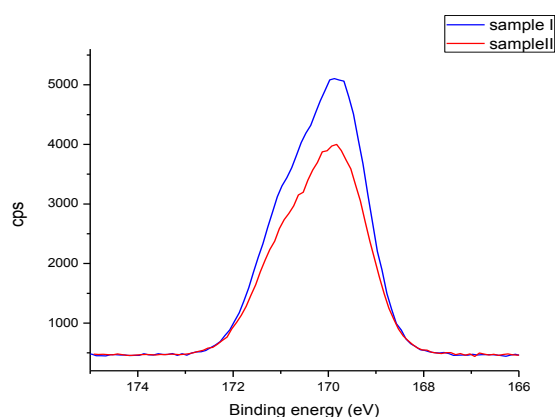


Figure 5. XPS S 2p Spectra of the Catalysts

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. 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<sub>1/2</sub> and 2p<sub>3/2</sub>, respectively. These binding energies correspond to sulphur in sulphate in agreement with other reported data in literature [10]. Clearly, the O1s spectra for both samples were consistent as shown in Figure 6, indicating the presence of S<sup>6+</sup> in SO<sub>4</sub><sup>2-</sup>. 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 [1, 10] were observed. 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.

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

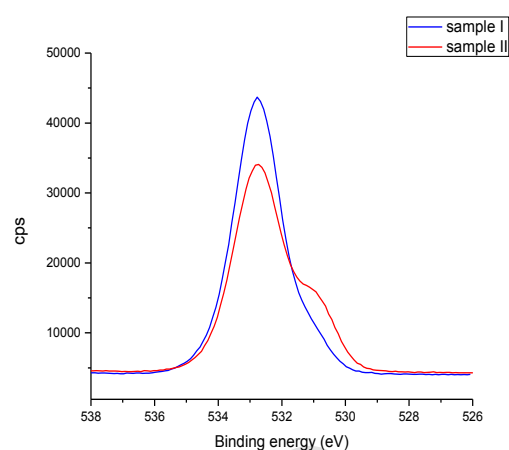


Figure 6: XPS O 1s Spectra of the Catalysts

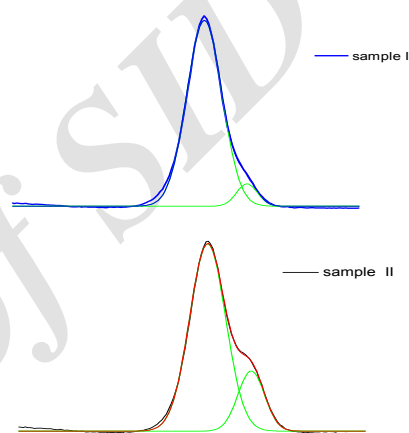


Figure 6: Deconvoluted O 1s Spectra of the Catalysts

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 [6], 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.

## 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 [1, 11] 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 other published researches. The non-aqueous preparation method resulted into amorphous, Brönsted-dominated catalysts in contrast to [7]. 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 zirconias is not necessarily required for Brönsted acid site formation. Also, sulphated zirconia catalyst with higher activity properties can be achieved via a non-aqueous, environmental benign method.

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## Persian Abstract

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### چکیده

کاتالیزورهای غیر کریستالی سولفات زیرکونیا با روش غیر آبی و غیر معمول سنتز شد. اثر تغییر نسبت مولی عامل سولفات به منبع زیرکونیوم نیز مورد بررسی قرار گرفت. نمونه ها به وسیله ی پراش اشعه ایکس، پراش انرژی اشعه ایکس، طیف سنجی مادون قرمز و طیف سنجی فوتوالکترون اشعه ایکس آنالیز شدند. اسیدیته ی سطح با استفاده از تکنیک پرییدین-DRIFTS (طیف سنجی بازتابی اشعه مادون قرمز) اندازه گیری شد. خواص ساختاری و بافتی زیرکونیا سولفاتی مورد مطالعه قرار گرفت. پروفایل های پراش انرژی اشعه ایکس و طیف سنجی فوتوالکترون اشعه ایکس هر دو پیشنهاد می کنند که کاتالیزورهای سولفید زیرکونیا دارای ساختارهای یکسان زیرکونی و سولفاتی هستند با این حال هر دو کاتالیزور غیر آمورف هستند. طیف سنجی فوتوالکترون اشعه ایکس نشان می دهد که نمونه ها حاوی هر دو اکسید اکسیژن زیرکونیوم و سولفات اکسیژن هستند و نمونه ی یک بیشترین مقدار از سولفات اکسیژن را نشان می دهد. جذب پرییدین در نمونه ها نشان می دهد که مقادیر بالاتری از اسید پرونسلد در نمونه یک، با مقدار کمتری از سولفات طی آماده سازی ارائه شده است. این امکان کنترل درجه و نوع سایت های فعال در یک کاتالیزور را با مقدار سولفات مورد استفاده برای آماده سازی نشیاز می کند. کاتالیزور زیرکونیوم سولفاتی با خواص فعالیت بالا از طریق روش غیر آبی دوستدار محیط زیست به دست می آید. کاتالیزور زیرکونیا سهم بزرگی در تولید انرژی برای آماده سازی و ترانس-استری کردن اسیدهای چرب برای تولید بایو دیزل دارد.