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

E. J. Eterigho¹, T. S. Farrow² and S. E. Ejigibe³

¹Chemical Engineering Department, Federal University of Technology, Minna, Niger State, Nigeria
²Chemical and Petroleum Engineering, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria
³Elm close off Rumuibekwe Road, Rumurolu Port Harcourt, River State, Nigeria

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 Brönsted 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, environment-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.

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 exhibits high activity and selectivity towards the production of the desired product(s). Several routes to synthesise 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 catalysts 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][4][5] among 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 Brönsted 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
concentrations of sulphur (< two ‘S’ atoms/nm$^2$) resulted in Lewis acidity, and higher concentration (> two ‘S’ atoms/nm$^2$) in Brønsted 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 Brønsted acidity. 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 AlKα1, 2 X-ray sources and charge neutraliser. Spectra were processed using CasaXPS 2.3.15 software, with energy referencing performed by setting the CHx 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 Kα radiation with a wavelength of λ = 1.54 Å generated at 40 kV and 40mA from 20C to 100oC. The BET surface areas were measured using the isothermal adsorption/desorption N2 at 77K using the CoulterTM SA 3100TM series. The samples were out gassed for 2h at 200°C prior to the analysis. The numbers of Brønsted and Lewis acid sites were calculated using the equation below.

$$N_T = \frac{A_L \times C_d}{\varepsilon_L \cdot m} + \frac{A_B \times C_d}{\varepsilon_B \cdot m} \quad (1)$$

where:
- NT is the total number of pyridine/g of sample adsorbed (µmol)
- AL/AB are the integrated absorbance (cm$^{-1}$) at Lewis (L) or Brønsted (B) sites
- Cd is the cross-sectional area (cm$^2$) of the pressed disk
- m is the mass (g) of the pressed disk, and
- εL/εB are the molar absorption coefficient for pyridine at Lewis (L) or Brønsted (B) sites (cm$\mu$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>
<thead>
<tr>
<th>Catalyst</th>
<th>BET (m$^2$/g)</th>
<th>O$_2$ of SO$_3^2$/ O$_2$ of Zr (from O1s in XPS)</th>
<th>Crystallite size (nm)</th>
<th>Elemental analysis (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Zr</td>
</tr>
<tr>
<td>Sample I</td>
<td>168</td>
<td>10.5</td>
<td>A</td>
<td>35.5</td>
</tr>
<tr>
<td>Sample II</td>
<td>102</td>
<td>3.2</td>
<td>A</td>
<td>42.1</td>
</tr>
</tbody>
</table>

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.

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 ($\delta$HOH) of coordinated water. The band at 1300 to 950 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 Brönsted 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 - 1500 cm$^{-1}$, which are assigned to adsorbed pyridine forming Lewis-type adducts. Also, a well-defined adsorption bands around 1510-1563 cm$^{-1}$ due to Brönsted acid sites. The absorbance of these bands varies. The intensity of the band between 1510 - 1563 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.

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 eV and 185.5 eV, respectively. However, the binding energy between the doublets was found to be the same (2.4 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
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 169.5 eV and another between 170/171 eV 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 reported data in literature \cite{10}. Clearly, the O1s spectra for both samples were consistent as shown in Figure 6, indicating the presence of S$^6$ in SO$_4^{2-}$. Oxide oxygen of the zirconia at binding energies of 530.5 eV/531.0 eV and 532.5 eV assigned to sulphate oxygen on the surface of the catalyst \cite{1, 10} were observed. The peak at 530.5 eV/531.0 eV is higher for sample II indicating higher Oxide oxygen. However, sample I exhibited higher peaks at binding energy 532.5 eV as shown in Figure 7, corresponding to sulphate oxygen which resulted into its higher Brønsted 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 oxychloride octahydrate to ammonium sulphate used in the preparation, which results in a remarkable level of Brønsted 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 \cite{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 \cite{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.

REFERENCES