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## Synthesis, characterisation of sulfated zirconia & application as solid acid catalyst for industrially important organic reaction

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### ABSTRACT

Sulfated zirconia can be considered as zirconium dioxide (zirconia) doped with sulfate. Its modification with various transition metals such as Pt<sup>[18]</sup>, Fe and Mn<sup>[19]</sup>, has been found to improve the catalytic activity and the stability against the rapid deactivation of sulfated zirconia. Sulfate-treated zirconia-gel modified by platinum is active for n-pentane isomerization and the activity as well as the selectivity being similar to those of commercial catalysts<sup>[1]</sup>. It can behave as a superacid on the basis of measurements of titration method of Hammett indicators<sup>[2]</sup>. In the present work A series of mesoporous sulfated zirconia (SZ) were synthesized and their catalytic activity has been measured in organic synthesis of cumarin, xanthene and flavanone. The catalysts has been characterized through XPRD studies, FT-IR Studies and their SEM morphology. © 2010 Trade Science Inc. - INDIA

### KEYWORDS

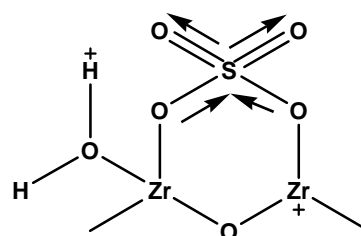
Sulfated zirconia;  
Catalytic activity;  
Selectivity;  
Mesoporous;  
Superacid;  
Doped.

### INTRODUCTION

Catalysts are chemical compounds that increase the rates of chemical reactions which are thermodynamically feasible, yet the catalysts are not themselves altered in any way by these reactions- Homogeneous catalysis refers to a reaction in which the catalyst itself is soluble in the reaction medium. Heterogeneous catalysis refers to reactions in which the catalyst is of a different phase than the medium in which the reactants are dispersed. sulfated zirconia was described as a superacid (more acidic than 100% H<sub>2</sub>SO<sub>4</sub>) based on its ability to isomerise n-butane at low temperatures and acidity measurements using Hammett indicators<sup>[2,3]</sup>. As for conventional sulfated zirconia various optimum sulfur contents have been reported, including: 170µg/m<sup>2</sup>

(3S atoms/nm), 1-2 wt.% S or 2.6 wt.% S. Zirconia occurs in three main polymorphs; Monoclinic, Tetragonal & cubic.

Sulfated zirconia can be regarded as a superacid on the basis of measurements with Hammett indicators which shows that the H<sub>0</sub> value of sulfated zirconia is lower than -14.52, and therefore, in the range of superacids. The sulfate groups on active sulfated zirconia present the bridging bidentate structure represented is the following;



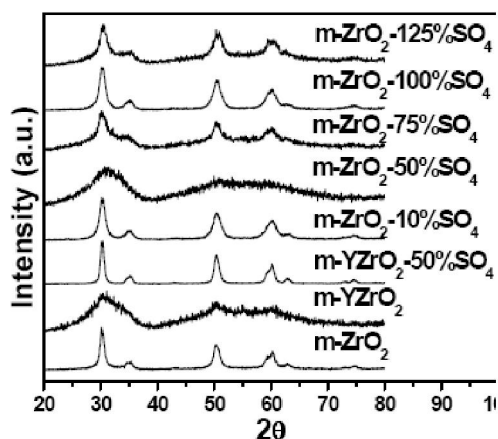


Figure 1 : XPRD spectra of sulphated zirconia

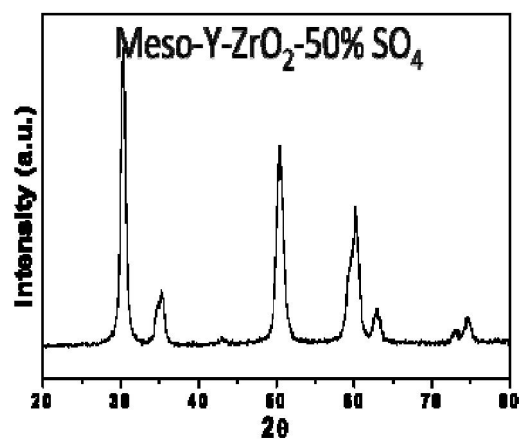


Figure 2 : XPRD spectra yttria-doped zirconia

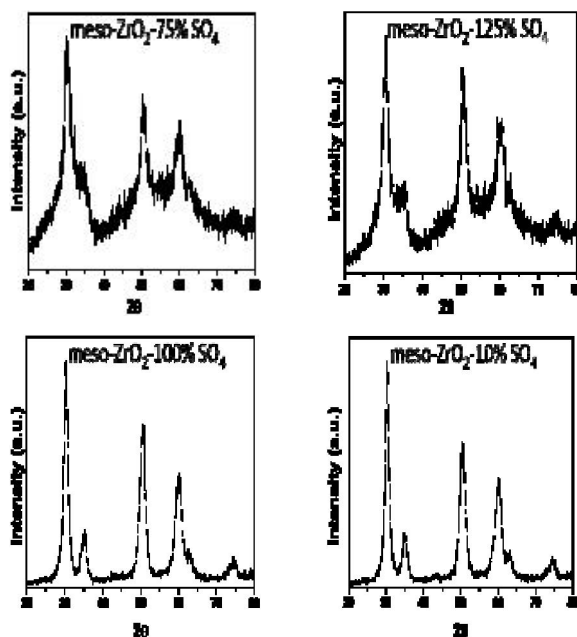


Figure 3 : XPRD spectra of sulphated zirconia

The sulfate groups on active sulphated zirconia present the bridging bidentate structure represented in Scheme 1. According to this model, the strength of Lewis acid sites  $Zr^{4+}$  is increased by the inductive effect of the sulfate groups in the complex. The model also demonstrated that it is possible to convert Lewis acid sites into Brønsted acid sites by water adsorption.

## EXPERIMENTAL

### Catalyst preparation

Reagents required are Zirconium oxychloride, Ammonium sulfate, CTAB (Zr : CTAB = 1:0.25), Distilled water (Zr:H<sub>2</sub>O = 1:1000).

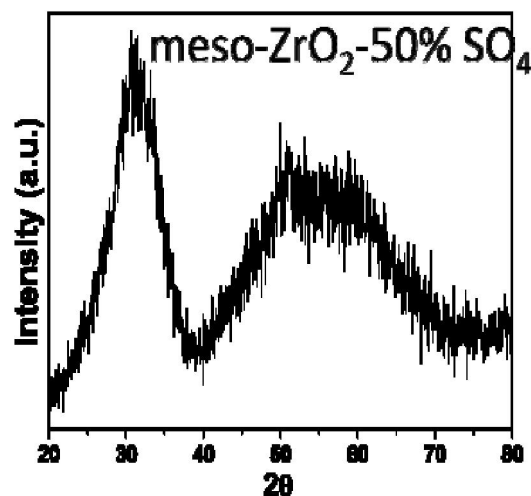


Figure 4 : XPRD spectra of sulphated zirconia (50%)

### Procedure

A solution of CTAB was prepared by dissolving 2.26gm of CTAB in water. The zirconia solution as well as the aqueous ammonium sulphate solution (0.08gm) were simultaneously added dropwise with constant stirring. The reaction mixture was kept for 12 hours at room temperature while stirring. The reaction mixture was transferred in glass-bottle and kept in oven at 80°C for 24 hours, then at 100°C for 24 hours. Next the solution was transferred into Teflon line autoclave and kept for at 100°C and 110°C for 24 hours for both cases. Finally, the precipitate was centrifuged from solution, washed well, dried at 100°C for 8 hours, and was then calcined at 550°C for 6 hours. That was designated as ZrO<sub>2</sub>-10% SO<sub>4</sub>. Similarly,

ZrO<sub>2</sub>-25% SO<sub>4</sub> (Zr/SO<sub>4</sub> = 1/0.25), ZrO<sub>2</sub>-50% SO<sub>4</sub> (Zr/SO<sub>4</sub> = 1/0.50), ZrO<sub>2</sub>-75% SO<sub>4</sub> (Zr/SO<sub>4</sub> = 1/0.75), ZrO<sub>2</sub>-100% SO<sub>4</sub> (Zr/SO<sub>4</sub> = 1/1), ZrO<sub>2</sub>-125% SO<sub>4</sub>

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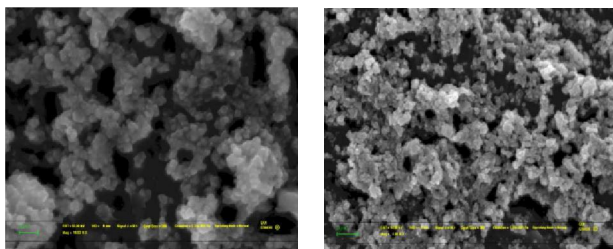


Figure 5 : SEM images of the sample ZrO<sub>2</sub>-25%SO<sub>4</sub>

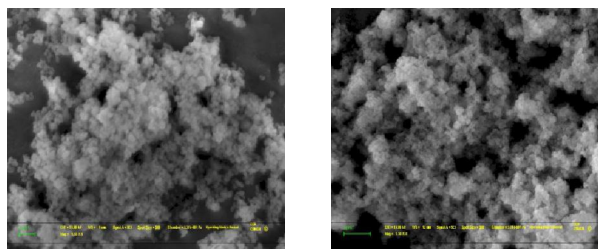


Figure 6 : SEM images of the sample ZrO<sub>2</sub>- 100%SO<sub>4</sub>

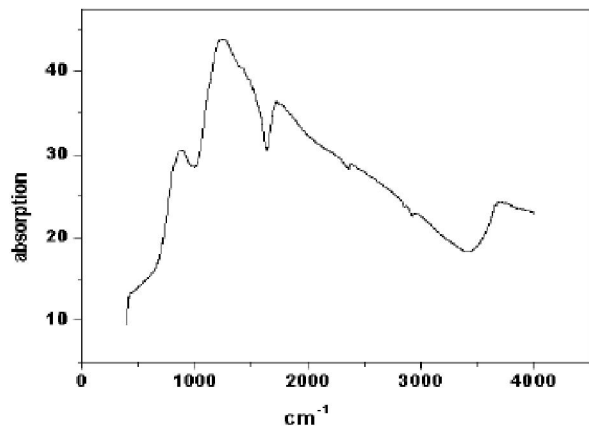


Figure 7 : FT-IR spectrum of ZrO<sub>2</sub> – 25% SO<sub>4</sub>

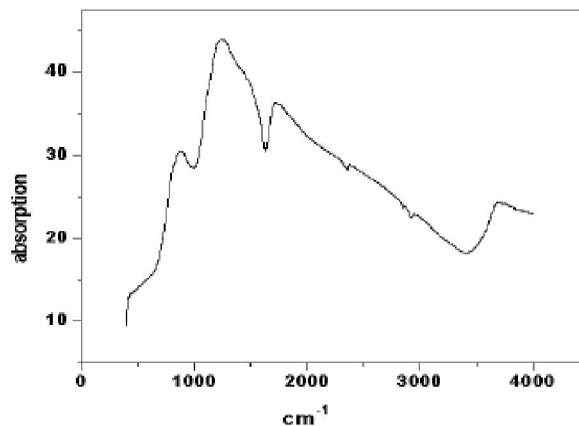


TABLE 1

Observed peak (cm <sup>-1</sup> )	Bond
1375-1385	Presence of sulfate species
1610-1630	OH bending mode of H <sub>2</sub> O
3650-3700	OH stretching of H <sub>2</sub> O

(Zr/SO<sub>4</sub> = 1/1.25), were prepared by changing the molar ratio between Zr and SO<sub>4</sub>.

Another series of yttrium incorporated sulphated zirconia were prepared using yttrium nitrate as the source of yttrium and were designated as YZrO<sub>2</sub> (where Zr/Y = 1/0.05) and YZrO<sub>2</sub>-50% SO<sub>4</sub> (where Zr/Y = 1/0.05, Zr/SO<sub>4</sub> = 1/0.5).

### Catalyst characterization

The sulfated zirconia samples were characterized by,

- Powder X-ray diffraction analysis for the phase identification in the range of 20 to 80 2θ using X'pert MPD system, Philips, Holland.
- FTIR spectra were recorded on Perkin Elmer GX (USA), spectrophotometer.
- Scanning electron microscopy (LEO 1430 VP) of the samples was done for the study of particle morphology of the samples.

### X-ray powder diffraction studies

Powder X-ray diffraction patterns of the sulphated

TABLE 2 : Catalytic activity of the catalyst in different reaction

Reaction	%Conversion
Pechman reaction	84.76
Xanthene synthesis	92.11
Flavanone synthesis	74.90

zirconia samples along with yttrium incorporated sulfated zirconia are shown in figure 1. The wide angle XRD patterns show three prominent peaks at 2θ = ~30°, ~50° and ~60° which correspond to 111, 220, 311 reflections respectively of tetragonal crystalline zirconia phase. A small hump at 35° corresponds to 200 reflection, of monoclinic phase of zirconia. Sulfated zirconia having two different Zr/SO<sub>4</sub> ratio (Zr/SO<sub>4</sub> = 1/0.75 and 1/1.25) were found to be highly crystalline materials with very intense characteristic peaks of tetragonal zirconia phase. In the sulfated zirconia samples, it can be seen that as concentration of SO<sub>4</sub> increases the crystallinity of the sample increased. On the other hand this result is also revealed by the yttria-doped zirconia where in presence of SO<sub>4</sub> the crystallinity increased.

### FT-IR studies

The Figures show the IR spectra of various mesoporous sulfated silica zirconia samples with various SO<sub>4</sub> content. This table gives the peaks correspond-

ing to the bonds present in the sample. The peak that ranges between 1375-1385 $\text{cm}^{-1}$  corresponds to the presence of  $\text{SO}_4$  in the samples.

### Sem morphology

The following figures describe the SEM morphologies of two sulfated zirconia samples. In all the SEM images circular morphology was quite visible and rapid clustering was also present in each images.

### Catalytic activity

Three different types of reactions were carried out using the catalyst  $\text{ZrO}_2$ -50% $\text{SO}_4$  and corresponding % conversion were given in the following table. The high % conversion value reveals that the catalyst behaves as a good solid acid catalyst. After completion of reaction, The catalyst was separated by centrifuge and a part of the solution containing the product was sent for GCMS.

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