Preparation and Characterization of Sulphated Zirconia Catalyst Precipitated in Acidic Medium

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Abstract: Recently, sulphated zirconia has been widely studied, particularly its potential application as solid catalysts in acid catalyzed reactions. In addition, sulphated zirconia has oxidizing properties which may play a role in synthesis of organic compounds. The aim of this work is to prepare a series of SO_4/ZrO_2 catalysts precipitated by different sulphuric acid concentrations using sol gel preparation method. The prepared catalysts were calcined at 450, 550, 650, 800 ^{o}C. The surface acidity of the prepared catalysts was measured by n-butylamine method, and by pyridine adsorption. Sulphated zirconia tetragonal phase was successfully prepared in acidic medium using 2N H_2SO_4. It was observed that increasing of the calcination temperatures was associated with transformation of amorphous phase to crystalline phase. The incorporation of sulphate ions into ZrO_2, increased the surface acidity of the catalysts. Moreover, the acidity was found to increase with increasing the calcination temperature from 450 to 650 ^{o}C and then decreased. The surface area was found to increase with increasing of SO_4/ZrO_2 ratio upto 15% and then decreased. Also, the surface area was found to increase upto 550°C and then decreased. The precipitation of hydrous zirconia in acidic medium followed by calcination, produces solid materials with useful properties that favor their application in catalysis. The activity of these catalysts were tested for synthesis of 7-hydroxy 4- methyl cumarin. Usually the higher activity of these catalysts was attributed to its higher acidity.

1. Introduction:

Pechman condensation of phenols with keto esters to prepare cumarin and its derivatives has been known to be an important process, during which sulphuric acid is most frequently employed as catalyst (Potrdar et al., 2001). Cumarin belongs to the benzopyrone class of compounds that are present in many natural products, and have a great biological importance, many cumarin derivatives act as antibiotics.

This process is associated with problems of corrosion, large catalysts amounts, difficulties in the separation of the catalyst, solid acid catalysts such as, zeolites, clays, and sulfonic acid resins (delaude et al., 1993; Holderich and Bekkum, 1991).

Recently, zirconium oxide and compounds containing zirconium are increasingly being recognized as useful catalytic materials(Luo et al., 2005). Particularly, zirconium oxide (zirconia) is an important supporting material for catalysts having both acidic and basic properties(Chuah et al., 1996). Zirconia has an additional advantage that the nature of the active sites is known and may be defined by the generating Bronested and Lewis acid sites. In light of recent studies, many preparation methods have been explored to obtain the superfine ZrO_2 powders, such as hydrothermal process, vapor phase hydrolysis, sol gel process, and combustion methods (Ray et al., 2002).

It has also reported that sulfated zirconia has attracted considerable interest and was intensively studied in the last 20 years (Yamaguchi et al., 1990). So far, it is recognized as a very strong acid and possesses all the advantages of heterogeneous catalysts, such as easy separation, recovery and reutilization. Moreover, various recent works confirm that the acidity of sulphated zirconia is not stronger than the acidity of pure sulphuric acid (Babou et al., 1994; Babou et al., 1995).

This material exhibits high catalytic activity in a number of industrially important reactions (Zhao et al., 2008).

Sulphate-doped zirconia samples have also attracted great interest, due to their strong acid characteristics, and their potential as solid acid catalysts for selective hydrocarbon isomerisation and several other acid-promoted reactions. In this way sulphated zirconia was classically synthesized by precipitation of zirconium hydroxide by hydrolysis of $ZrOCl_2$ aqueous salt solutions (Morterra et al., 1994; Melada et al., 2004; Li et al., 2006).

It's now well known that, sol gel template method is a popular one because of its distinctive advantages such as the high purity, the

homogeneous multi component and the easy chemical doping of the prepared materials (Yang et al., 2005, 2006). So far, this method typically entails hydrolysis of a solution to obtain a colloidal particles (sol) and then a gel is formed. The latter point is of a particular importance for surface area of zirconia as usually rather low, in order 20 - 50 m^2/g. Different routes to obtain zirconia with high

surface area have been reported (Ozawa et al., 1990; Ciesla et al., 1996).

However, most of the reported catalysts suffer from various drawbacks such as long reaction times, and some of the reagents used are expensive. In this study, we employed the promoted ZrO$_2$ catalysts for the synthesis of substituted cumarin from resorcinol and substituted resorcinol with ethyl acetoacetate (Scheme 1) (Reddy et al.,2001; Reddy et al., 2005).
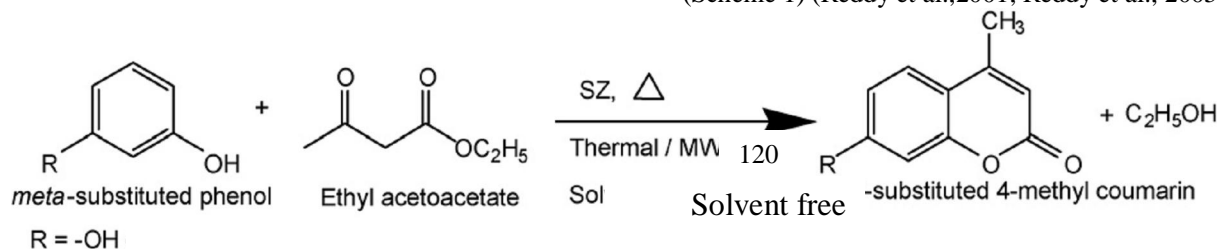
Scheme (1). Schematic synthesis of 7-substituted 4-methyl cumarin.

We conducted a test: A solvent free Pechman reaction mixture was irradiated with microwaves of low power. The temperature of the reaction mixture started to rise. After 20 min of irradiation, the microwave oven was switched off. The reaction mixture continued to rise in temperature after addition the catalyst (Manhas et al., 2006). The reaction was completed in less than 10 min (monitored by TLC). The target cumarin was isolated. This new energy-saving procedure was found to be useful for the efficient preparation of several cumarins.

The aim of the present work is to bring new evidences concerning the role played by the sol gel preparative variables, and surface features of sulphated zirconia catalysts, as well as the effect of the type of starting salts on the sol gel method. Additionally trying to establish the correlation between the catalytic properties of sulphated zirconia samples calcined between 450 - 800°C and their acidic properties.

2. Material and Methods

Zirconium hydroxide was prepared by sol gel method from zirconium oxy chloride salt dissolved in ethanol (Dominguez al., 2000) and precipitated

by adding a drop wise of H$_2$SO$_4$ (analar) with vigorous stirring. These gels were dried at 120 ^{o}C for 24 hrs, to obtain the powder from sulphated zirconia, followed by the calcination at different temperatures (450, 550, 650, 800°C) for 3 hrs.

In the designation of these samples, the letters S, Z denotes to SO$_4$ and ZrO$_2$ respectively. The roman numbers I, II, III, and IV referred to the calcination temperature. While the Arabic numbers 1, 2, 3 and 4 represents SO$_4$ concentration. The designation 2SZI indicates, the sample precipitate by 2N H$_2$SO$_4$, and calcined at 450 ^{o}C.

Thermal analysis (TGA) of the uncalcined samples was carried out using a Shimadzu thermal analyzer, type 50-H. The samples under examination being heated in N$_2$ stream at a rate of 10 ^{o}C/min throughout.

X-ray diffraction patterns of the calcined samples were recorded using a Philips PW 105 diffractometer using Ni-filtered Cu Ka radiation (=1.540 A ˚) at 40 kV, 30 mA, and a scanning range 2hrs of 18-80°. The percentage of zirconia tetragonal phase was estimated with the following formula (Devassy et al., 2005)

$$\% \textbf{ Tetragonal} = \left[\frac{IT(2\theta = 30.15)}{IT(2\theta = 30.15) + \left(\frac{IM(2\theta = 28.16) + IM(2\theta = 31.44)}{2} \right)} \right] \times 100$$

The crystallite size (nm) was calculated from the reflection of tetragonal zirconia phase at 2hrs of

30.15, using the Scherer relationship (patterson, 1939)

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where k is the crystallite shape constant (1),   is the radiation wavelength (A˚),   is the line breadth (radians) and   is the Bragg angle.

The specific surface areas of the calcined samples were determined from nitrogen adsorption studies conducted at -196°C using the high vacuum conventional volumetric glass system (BET). Prior to any adsorption measurement, the sample was degassed at 250 ^{o}C for 3 hrs under a reduced pressure of 10^{-5} Torr.

The total acidity of all catalysts was determined by means of the n-butyl amine titration method (Suryanarayana et al., 2006; Ahmed et al., 2007) , using an orion 420 digital model using a double junction electrode. In this method, 0.2 gm catalyst was heated under vacuum, then 10 ml of acetonitrile was added. After agitation for 2 hrs, the suspension was titrated by 0.01 N. n-butyl amine in acetonitrile. The addition is continued till no further change of mv recorded.

The FTIR spectra of the samples were carried out at room temperature. 0.05 gram of each sample was degassed for about 2 hrs at 250 C to reduce the amount of adsorbed molecular water. The samples were maintained in contact with pyridine vapor, at room temperature, for one week, after that 0.05gram of the sample is mixed with 0.1 gram of KBr in a 30 mm diameter self supporting discs.   The FTIR spectra of the 0.05 gram of samples were recorded at room temperature in region 1700-1400 cm^{-1}. (Mohamed et al., 2000)

The catalytic activity of the investigated samples towards peckman condensation reaction was studied. In a typical experiment, a mixture of resorcinol (1.1 gram, 10 mmol) and ethyl acetoacetate (2.5 ml, 20 mmol) was added in a 50 ml round flask. This reaction mixture was placed in oil bath and refluxed for 2hrs at 120˚C (Sethna et al., 1953; shockravib et al., 2005). At the same time, (0.1 gram) of catalyst was activated at 120˚C in oven, then added to the reaction mixture and refluxed continuously for another 2 hrs. Finally, the reaction mixture was allowed to cool down to room temperature by pouring the reaction mixture at 50ml beaker containing crushed ice. The product 7-hydroxy-4-methyl cumarin was separated, tested and characterized by its melting point and FT-IR spectroscopy.   The yield (wt%) was obtained as follows (Tyagi et al., 2008) :

$$yield \ (wt \ \%) = \frac{obtained \ weight \ of \ product}{theoritical \ weight \ of \ product} \ x \ 100$$

3. Results:

X-ray diffraction: Zirconia precipitated by sulphuric acid samples were investigated to confirm the effect of sulphate group presence on the surface area and on the tetragonal phase of zirconia. The phase composition and the crystallites sizes were determined for all the precursors and calcined samples. Figures 1, 2 and table 1 show the effect of the variation of the concentration of sulphuric acid, and the calcination temperature on the crystal size and the percentage of tetragonal phase respectively. The results show that the tetragonal phase increases by increasing the sulphate content upto 15% and then decreases. While by increasing the calcination temperature the phase changes from amorphous to crystalline (tetragonal and monoclinic) phases.

Thermo gravimetrical analysis: Figure 3 shows three main weight loss regions. The first centered at about 100°C, due to the physisorbed water.   The second in the range 150–350°C, suggesting that beside the dehydration and dehydroxylation processes, elimination of carbonaceous species from the surface occurred.   The third at 570 - 800°C, associated to the amount of sulphate introduced during the sol gel synthesis.

Surface   characterization   by   nitrogen physisorption: The BET analyses of all the samples give isotherms of type II, with hysteresis loop of type H3 or H4 of the IUPAC classification, which is characteristic of slit-shaped pores. The first remark concerning the morphology deals with the surface area of the samples. Figures 4 , 5 and table 2 show the effect of both the concentration of sulphate and the calcination temperature on the surface area, respectively.   Figure 6 shows the pore size distribution in order to determine the types and the distribution of the pores. The results show that the surface area increased by increasing the sulphate content up to 15% and then decreases. While by increasing the calcination temperature the surface area increases upto 550 ^{o}C and then decreases.

Surface acidity: The surface acidity of the investigated catalysts was determined by non aqueous titration of n-butyl amine (pKa=10.73), which is a basic molecule suitable for titrating the medium and strong acid sites on the surface of the investigated catalysts (Pecchi and cid, 1985). Figure 7 illustrates the variation of the electrode potential for the investigated catalysts calcined at 650 ˚C with volume added from n-butyl amine.This figure shows that, as the acid sites of the solid become neutralized, a buffer behavior becomes more apparent.   The trend of the titration curve is asymptotic, leading to a characteristic value on the potential (mV) axis. This is related to the volume added from n-butyl amine / g needed for neutralization of the surface acidity (Dominguez. et al., 2000). The magnitude of

change of the electrode potential in this method is related to the surface acidity of the catalyst (Barrett et al., 1951). Table 3 shows the volume of n-butyl amine /g needed for the neutralization of the surface acidity of catalysts and the total number of acid sites /g. This technique was carried out by measuring the electrode potential (mV) as a function of the progressive increase of the   n-butyl amine concentration expressed as (mmol n-butyl amine / g catalyst). The total number of acid sites /g of the catalysts were calculated from the following relation:

Total number of acid sites / g = (ml equiv./g) $\times$ N $\times$ 1000 (Where N is Avogadro's number).

Figure 8 shows that sulfated zirconia samples contain mixture of Bronested and Lewis acid sites. The number of Bronested and Lewis acid sites were calculated from adsorption of pyridine. The Bronested and Lewis acidity were calculated and quantified from integrated areas of the absorbance bands at 1541 and 1446 cm^{-1}, respectively. Advantages of this technique are : Bronested (B) and Lewis (L) acid sites can be distinguished

because the IR spectra of adsorbed pyridine shows characteristic difference (Tanabe, 1970). The fact that the spectrum of pyridine coordinately bonded to the surface permits the differentiation between acid types on the surface of a solid acid (Parry, 1963). It is well known that the shift in the band wave number to higher values indicates that the strength of the acid sites increases, in contrast, the shift to lower wave number indicates that, the strength of the acid site decreases.

Catalytic activity for synthesis of cumarin: Table 4 shows that, Packman reaction depends mainly on the acidity of the catalysts (number of bronested and Lewis acid sites) which characterized using (FT-IR).

Figures 9 and 10 show the correlation between number of acid sites and the cumarin % with the variation of the sulphuric acid concentration, and the cumarin % with the calcination temperature. The results show that by increasing the sulphate content the acidity and cumarin % increases.   While by increasing the calcination temperature the acidity and cumarin % increased up to 650°C and then decreased.

Table 1: Phases identified by XRD, as a function of SZ calcined at 650°C and as a function of different calcination Temperatures for 2SZ samples

Samples	Crystal size nm	Tetragonal %	Samples	Crystal size	Tetragonal%
1SZIII	17	53.62	2SZI	Amorphous	-
2SZIII	25.8	82.11	2SZII	Amorphous	-
3SZIII	23.3	76.69	2SZIII	25.8	82.11
4SZIII	16.5	63.39	2SZIV	47.7	51.34

**Table 2 :Textural parameters of the catalysts investigated as evaluated from N$_2$ adsorption at -196 ^{o}C**

Samples	S_{BET} m^2/g	S_s m^2/g	S_T m^2/g	r$^-$ A^o	V_T ml/g
1N SZ 450	41.14	41.05	41.21	36.9	0.069
2N SZ 450	60.36	58.20	61.1	38.70	0.117
3N SZ 450	51.01	50.80	51.10	34.90	0.085
4N SZ 450	38.09	38.11	37.89	36.0	0.057
1N SZ 550	73.87	73.76	74.60	37.94	0.140
2N SZ 550	97.54	94.82	90.50	38.64	0.188
3N SZ 550	89.02	89.52	83.3	34.98	0.156
4N SZ 550	71.71	68.89	69.1	35.62	0.128
1N SZ 650	64.12	63.99	64.08	43.20	0.130
2N SZ 650	81.38	79.41	80.10	44.0	0.179
3N SZ 650	73.12	73.01	73.15	40.20	0.147
4N SZ 650	55.00	54.91	54.98	41.80	0.119
1N SZ 800	30.1	30.05	30.08	17.89	0.0170
2N SZ 800	51.11	50.99	51.01	18.28	0.047
3N SZ 800	44.31	44.20	44.25	14.50	0.015
4N SZ 800	24.30	24.22	24.29	15.10	0.008

Table 3 :Acidity parameters of the investigated catalysts:

Samples	No^o. of Acid sites x 10^{-18}	No^o. of lewis acid sites x 10^{-18}	No^o. of Bronested acid sites x 10^{-18}
1SZIII	2.41	0.96	1.36
2SZIII	3.01	1.05	1.70
3SZIII	3.14	1.35	2.00
4SZIII	3.207	1.45	2.22
2SZI	2.28	0.89	1.38
2SZII	2.67	0.99	1.56
2SZIII	3.01	1.05	2.00
2SZIV	2.35	2.20	-

Table 4: Effect of concentration and calcination temperature on the cumarin conversion %

Samples	Cumarin % by microwave	Cumarin % by simple method
1SZIII	10.89	11.12
2SZIII	20.50	21.15
3SZIII	26.79	27.20
4SZIII	39.88	40.87
2SZI	11.01	11.38
2SZII	16.85	17.43
2SZIII	20.83	21.15
2SZIV	11.42	11.60
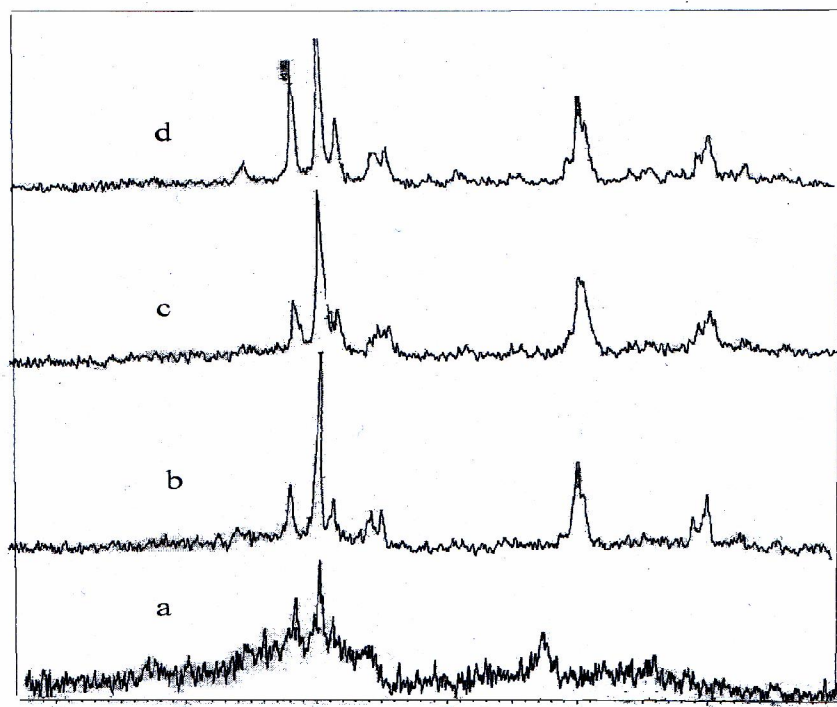
Fig. 1: X-ray diffraction patterns of the different SZIII concentration, (a)1SZ III, (b)2SZ III, (c) 3SZ III, (d) 4SZ III
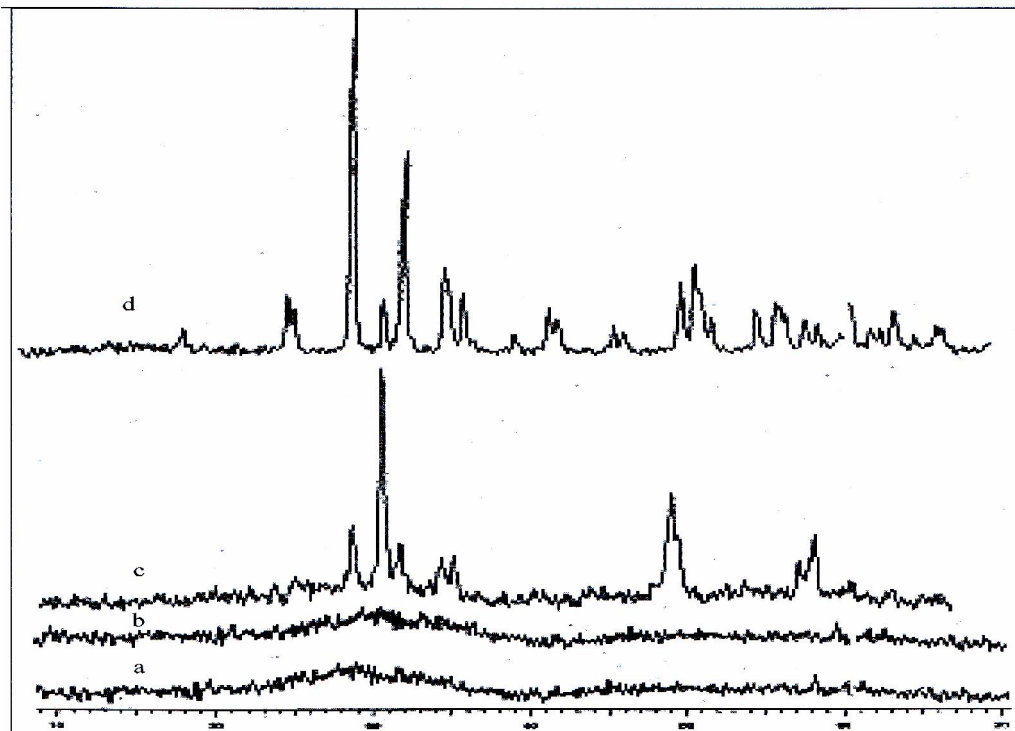
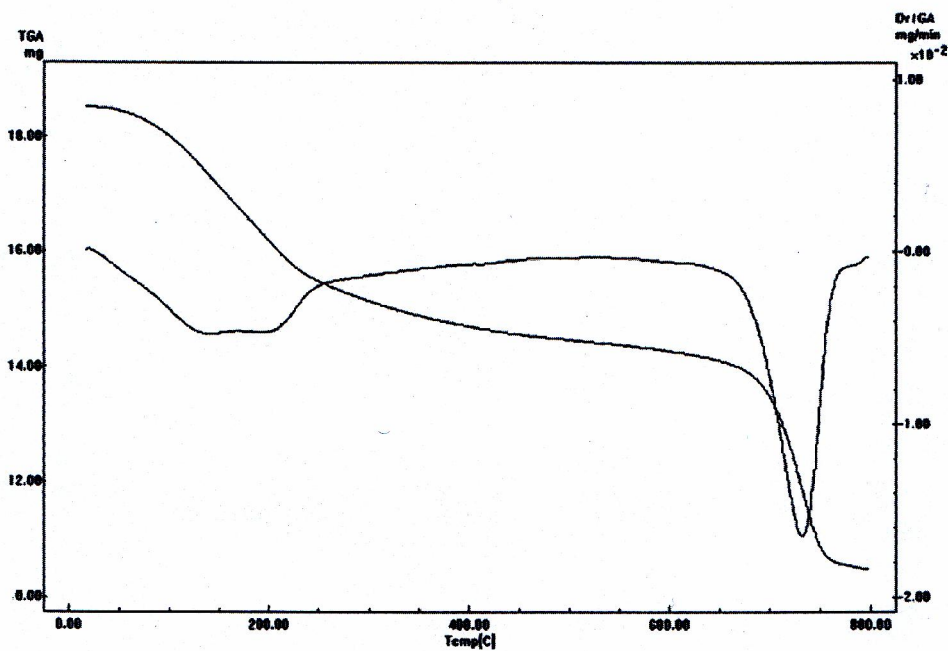**Fig. 2: X-ray diffraction patterns of 2SZ samples calcined at (a) 450°C,(b) 550°C, (c) 650°C, (d) 800°C**

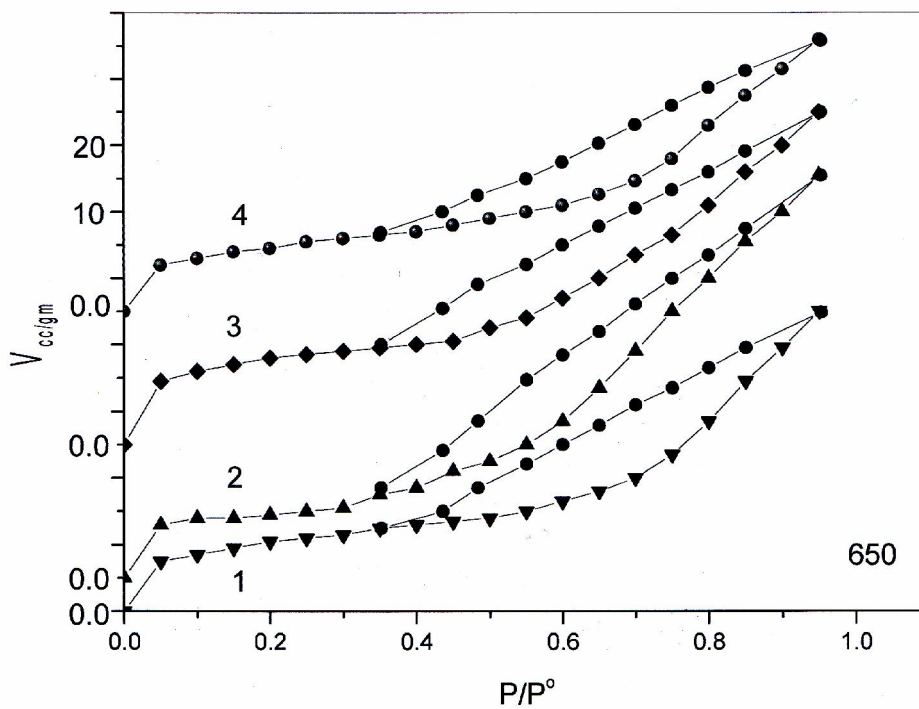**Fig. 3 : Thermogravimetric and Derivative Thermogravemetric Curves for 2NSZ**

Fig. 4 : Adsorption – desorption Isotherms of Nitrogen at -196ºC, on different SO$_4$ concentration for samples calcined at 650ºC
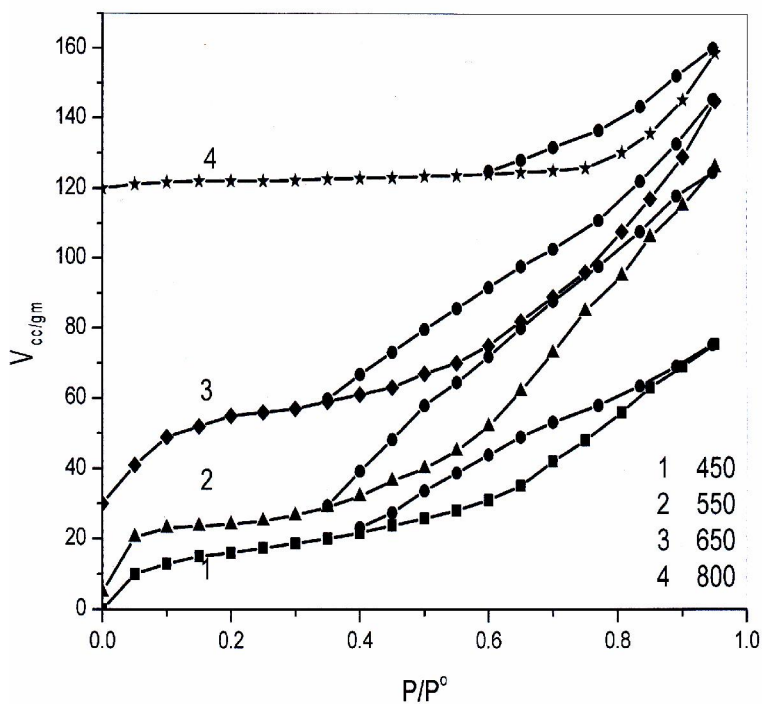

Fig. 5: Adsorption – desorption Isotherms of Nitrogen at -196ºC, on different Calcination temperature for samples at concentration 2N
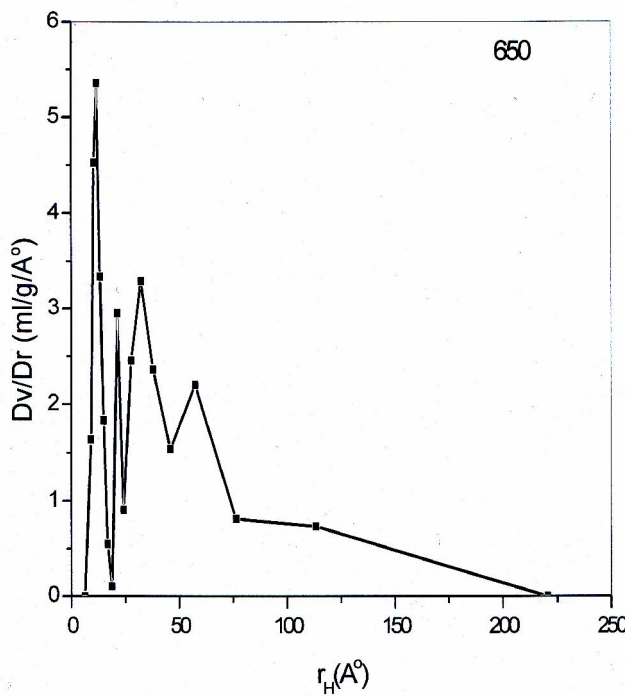
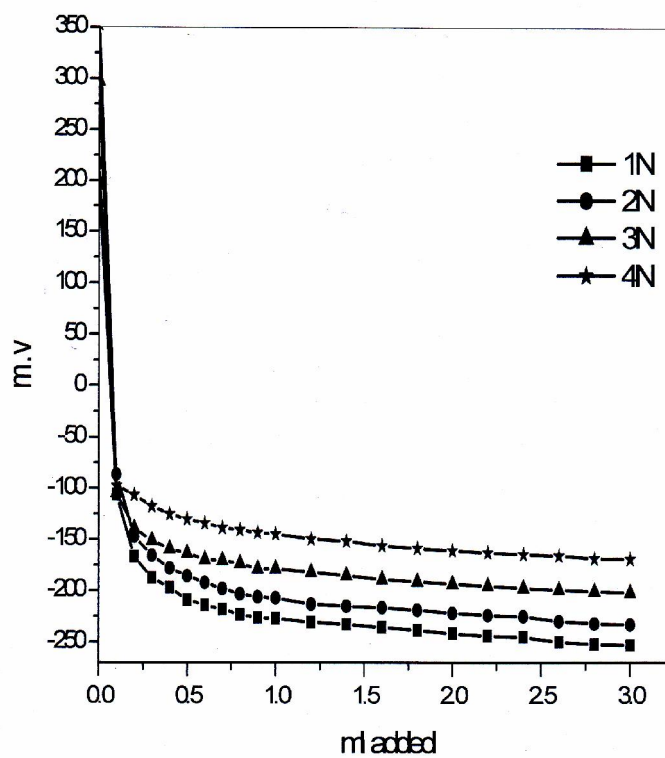**Fig 6 : Pore volume distribution for sample calcined at 650 ^{o}C**

Fig. 7 : potentiometric titration curve for sample calcined at 650 ^{o}C
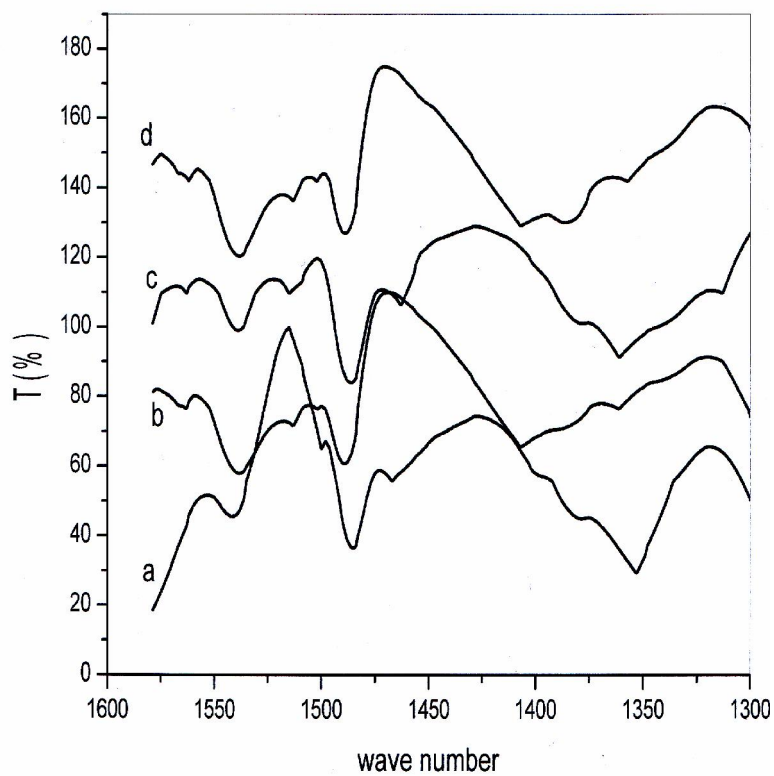
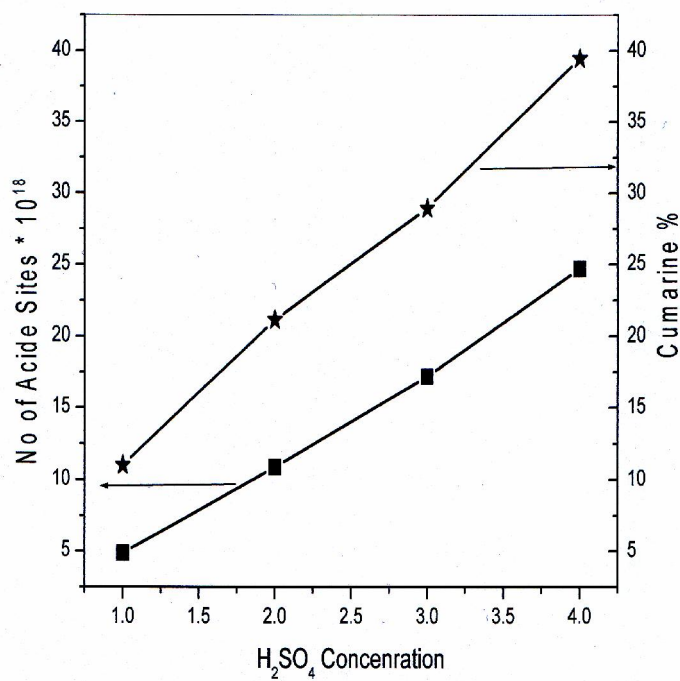**Fig. 8. FT-IR spectra of pyridine adsorbed of the different SZIII concentration, (a) 1N,(b) 2N, (c) 3N, (d) 4N.**

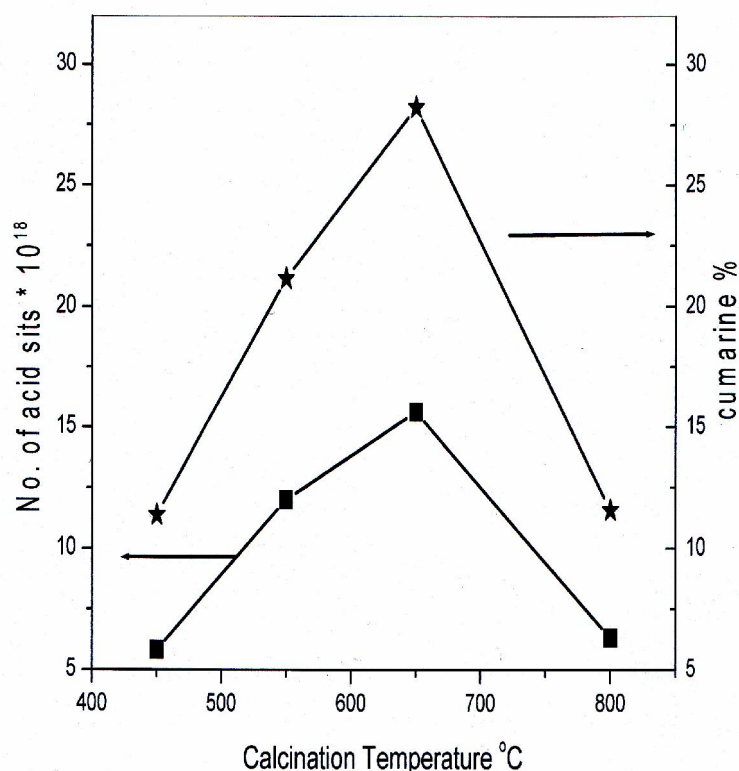**Fig. 9: Correlation between No. of acid sites and Cumarine%**

Fig. 10 : Correlation between No. of acid sites and Cumarine%

4. Discussion:

The obtained x-ray data shows the importance of the sulphate introduction step in the crystal phase development of sulphated zirconia. This feature could be explained on the basis of sulphate in stabilizing the tetragonal polymorph (Babou et al., 1994) and delaying the growth of zirconia crystallites (Babou et al., 1995). Increasing the concentration of SO_4^{2-} upto15%, the tetragonal phase increases.

All the sample precursors calcined below 650°C are amorphous. While the samples calcined above 650°C begin to crystallize, and the monoclinic (2 = 28° and 31 °) and tetragonal (2 = 30 °) phases appear.

It is clear from the nitrogen adsorption desorption isotherms that, by the increase of the concentration of sulphuric acid surface area increases upto 15%, and then decreased. This can be attributed to the increase in sulphate concentration which blocks the active sites on the surface. This was interpreted by the X-ray where, the tetragonal phase increases with increase of the sulphuric acid up to 15% and then decreases. On the other hand, the surface area was found to increase by the increase of the calcination temperature upto 550 °C and then decreased. This is

illustrated also by the X- Ray data. The samples calcined at 450 and 550 °C are amorphous, which show relatively higher surface area. While by increasing the calcinations temperature over 650 °C, the surface area decreases, which may be attributed to the sintering process and the grain growth of the pores.

It was clear from the potentiometric titration curves that the number of acid sites increases with the increase of sulphuric acid concentration. This could be attributed to the number of SO_4^{2-} groups bonded to the zirconia surface. So SO_4^{2-} / ZrO_2 interaction could be responsible for the acidity of the catalysts.

The results of calcination temperature on the surface acidity indicate that, the optimum temperature is 650°C. Further increase in calcination temperature to 800°C leads to notable decrease in the total acidity. This may be due to evolution of SO_3 gas as a result of decomposition of the sulfate groups bonded to the surface of zirconia .

The pyridine adsorption technique, enables us to evaluated the surface and the bulk acidity, because of the high absorptivity of sulfated acid catalyst to polar molecules as pyridine (Devassy, 2005; De Castro et. Al., 1998; Sun et al., 2002). In addition to the reaction with the surface protons, pyridine also

penetrates and reacts with the bulk acid sites of sulphated zirconia. The integrated area   of pyridine bands is a measure of number of Bronested and Lewis acid sites. The intensity of Bronested band (1541 cm^{-1}) and that for Lewis (1446 cm^{-1}) changed as the sulphate concentration on zirconia and the calcination temperatures changed.

Sulfated groups generate strong Lewis and Bronested acidity when adsorbed on the surface of sulphated zirconia. Sulfate species are itself Lewis acid sites or by attracting electrons, they generated Lewis acid centers on the oxide surface. Moreover, the chemical state of the sulfate groups sometimes determines the acidity of the oxide surface (Das et al., 2003). These results indicate that, the number of sulfate groups distributed on the surface of zirconia is maximum and responsible for the maximum acidity reaches at 650°C. At calcination temperatures higher than 650°C, the sulfate groups on the surface of zirconia decompose and thus the surface acidity decreases.

It's clear that from the activity measurement by cumarin conversion, and acidity measurements, the increase of H$_2$SO$_4$ concentration, increases both the acidity and the catalytic activity. Moreover, the activity increases by increasing the calcinations temperature upto 650 °C and then decreases. This may be attributed to the decomposition of the sulphate group after 650°C and its evolution as SO$_x$.

5. Conclusion:

On the basis of the above finding, the following are the main points that can be summarized: The increase in sulphate concentration in zirconia samples, the tetragonal phase increases by increasing the concentration upto   15% and then decreases. The samples calcined at 450-550°C are totally amorphous or poorly crystalline.   The rise of calcination temperature resulted in appearance of tetragonal and monoclinic phases.   The increase in sulphate concentration leads to a continuous increase of S$_{BET}$ upto 15%. Further increase of H$_2$SO$_4$ concentration decreases the S$_{BET}$. One can attribute the change of surface area of samples investigated to its capability to control zirconia phase transition and sintering of support.   SO$_4^{2-}$ / ZrO$_2$ interaction as well as the calcination temperatures will be responsible for acidity.   As the rise of H$_2$SO$_4$ concentration the acidity increases, this is due to the increase of SO$_4$ group. Also as calcination temperature increases the acidity increases up to 650 °C and then decreases. This due to above 650 °C the SO$_4$ decompose and went as SO$_x$. The increase of surface acidity was associated with an increase of cumarin conversion up to 650 °C and then decreased.

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