

# Synthesis, Characterization and Catalytic Activity Cobalt Doped Nano Sulphated Zirconia Catalyst: A Study of Cumarin Pechman Synthesis

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**Abstract:** A series of sulphated zirconia doped by cobalt oxide (CoSZ) catalysts were prepared. The structural characteristics were investigated by means of powder X-ray diffraction (XRD) Scanning electron microscope (SEM) and transmission electron microscope (TEM) while the textural properties were determined from low temperature adsorption of N<sub>2</sub> at -196 °C. The surface acidity was measured with non aqueous titration of n-butylamine in acetonitrile. The catalytic activity of the prepared catalysts was tested by Pechman condensation for production of cumarin. The XRD data indicated that, increasing Co content., the tetragonal phase increased up to 10 % Co, The surface area was found to increase with increasing of Co content upto 10% and then decreased, Also, by increasing Co content, the surface area was found to increase upto 600°C and then decreased. The incorporation of cobalt into SZ increases the surface acidity of the catalysts. Moreover, the acidity was found to increase with increasing the calcinations temperature from 400 to 600 °C and then decreased. The activities of these catalysts were tested for synthesis of 7-hydroxy 4-methyl cumarin (cumarin pechman synthesis). The higher activity of these catalysts was attributed to its higher acidity. It was concluded that, the catalytic activity was strongly influenced with the textural properties and surface acidities of the catalysts investigated.

**Keywords:** Cobalt doped sulphated zirconia; Characterization; Surface texturing; Acidity; Pechman synthesis.

## 1. Introduction

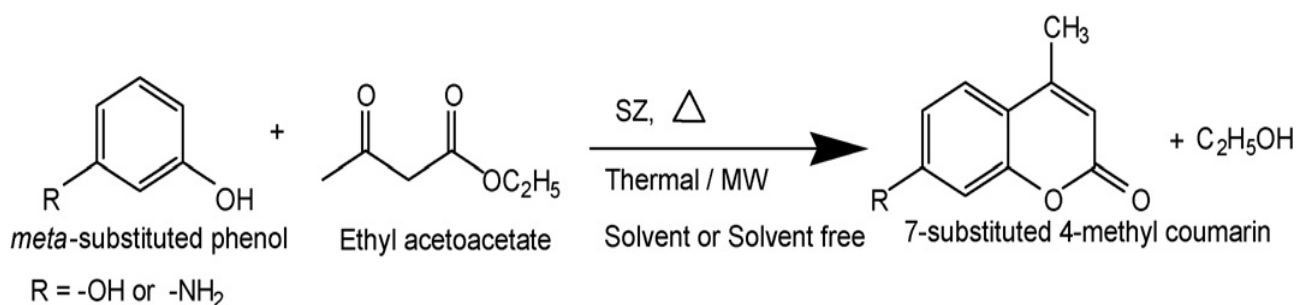
Recently, the superacids solid are an attractive option, which could replace the liquid acid used as catalysts in industry. Zirconium oxide and compounds containing zirconium are increasingly being recognized as useful catalytic material, particularly, zirconium oxide (zirconia) is an important support material for catalysis, having both acidic and basic properties [1]. Much more attention has recently been paid to Zirconia which has an additional advantage that the nature of the active sites is known and may be defined by the generated Brønsted and Lewis acid sites [2]. In light of recent studies, Many methods have been explored to obtain the superfine ZrO<sub>2</sub> powders, such as hydrothermal process, vapor phases hydrolysis, gas condensation, solgel process, and combustion methods [3,4].

It has also reported that sulfated zirconia has attracted considerable interest and was intensively studied in the last 20 years [5,6]. So far, it is recognized as very strong acid and possesses all the advantages of heterogeneous catalysts, such as easy separation, recovery and reutilization. This material exhibits high catalytic activity in a number of industrially important reactions [7,8]. In this way sulphated

zirconia was classically synthesized by precipitation of zirconium hydroxide from hydrolysis of Zr (NO<sub>3</sub>)<sub>2</sub> aqueous salt solutions [9,10].

Another way to control the properties of the sulphated inorganic oxides is the addition of other metals, producing mixed or doped systems. In particular, some metals can lead to more resistant against deactivation (11--15). Therefore, several metals such as platinum, palladium, iridium, iron, tungsten, nickel, and chromium have been added to sulphated zirconia, producing more active and selective catalysts[16].

In this work, intended to continue these studies, through the preparation and characterization of sulphated zirconia doped cobalt samples in order to gain a deeper insight into the essence of the CoSZ catalyst, which is responsible for the good catalytic performance of the catalyst, and to understand the promoting effect of Cobalt in Pechmann cumarin synthesis to produce 7- hydroxy 4-methyl cumarin. The prepared ZrO<sub>2</sub> catalysts will be applied for the synthesis of substituted cumarin from resorcinol and substituted resorcinol with ethyl acetoacetate (Scheme 1) [17,18]



Scheme (1). Schematic synthesis of 7-substituted 4-methyl coumarin

## 2. Experimental Procedure

### 2.1 Materials

The materials which used in our preparations are: Zirconyl nitrate, Pure sulphuric acid (2N), Cobalt nitrate.

### 2.2 Catalyst Preparation

Zirconium hydroxide was prepared with dropwise addition of H<sub>2</sub>SO<sub>4</sub> 2N to aqueous solution of Zr(NO<sub>3</sub>)<sub>2</sub> with vigorous stirring [19]. After gel formation, cobalt nitrate solution was added with different contents on gel to obtain (0%, 5%, 10%, 15%, and 20%) wt % Co on SZ samples. The precipitated gel was continuously stirred for 1hr after the precipitation has been completed. All of the prepared catalyst samples were dried at 120°C for about 3 hrs. The solid was pulverized and screened to 0.4-1.25 mm particle size. The prepared catalysts were calcined at 400, 500, 600, and 800°C.

### 2.3 Techniques

X-ray diffraction patterns of the calcined samples were recorded using a Philips PW 105 diffractometer using Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.540 \text{ \AA}$ ) at 40 kV, 30 mA, and a scanning range of 2 $\theta$  of 18-80°. The crystallite size (nm) was calculated from the reflection of tetragonal zirconia phase at 2 $\theta$  of 30.15, using the Scherrer relationship [20].  $D = K\lambda / \beta \cos\theta$

where  $k$  is the crystallite shape constant ( $\approx 1$ ),  $\lambda$  is the radiation wavelength ( $\text{\AA}$ ),  $\beta$  is the line breadth (radians) and  $\theta$  is the Bragg angle.

The total acidity of all catalysts was determined by means of the n-butyl amine titration method [21-23], using an Orion 420 digital A model using a double junction electrode. In this method 0.2 gm catalyst was heated under vacuum, then 10 ml of acetonitrile was added, and after agitation for 2 hours the suspension was titrated by 0.01 N. n-butyl amine in acetonitrile.

Transmission electron microscopy (TEM) was carried out using a JEOL 2010 instrument with resolving power 0.2 nm, accelerating tension being 200 keV. Reflectance UV-vis spectra were collected and converted to absorbance using a Perkin-Elmer Lambda 9 scanning spectrometer equipped with an integrating sphere over the spectral range 200-2500 nm (6.2-0.5 eV). The band gap energies quoted in this study are based on Shapiro's method 9 [24,25].

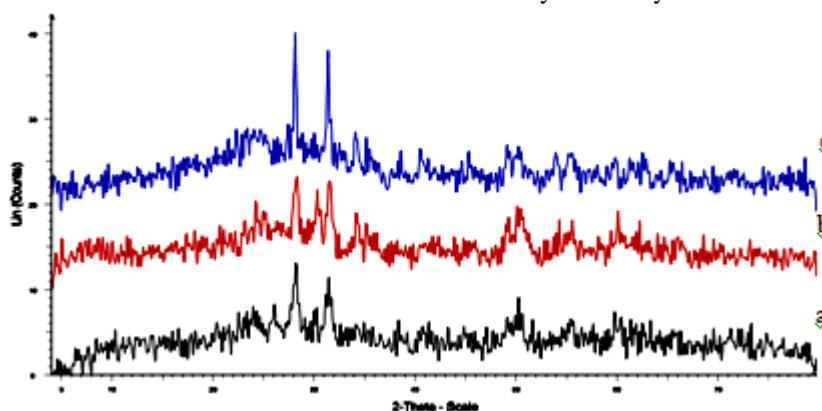
Particle sizes were examined by SEM on a Jeol JSM-840 under high vacuum, at an acceleration voltage of 200 kV. The samples were deposited onto carbon tape and coated with gold in a Blazers plasma sputtered (30s at 30mA).

A mixture of resorcinol (1.1 g, 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 2 hrs at 120°C, at the same time (0.1 g) of catalyst was activated at 120°C in oven then added to the reaction mixture and reflux continuous for another 2 hrs. The reaction mixture was allowed to cool down to room by pouring the reaction mixture at 50ml beaker containing crushed ice. The product 7-hydroxy-4-methyl coumarin separated was tested and characterized by its melting point and FT-IR spectroscopy. The yield (wt%) was obtained as follows [26].

$$\text{yield (wt\%)} = \frac{\text{obtained weight of product}}{\text{theoretical weight of product}} \times 100$$

## 3. Results and Discussion

The crystalline structure of CoSZ samples calcined in air at 600 °C were checked by XRD as shown in Figure (1). The X-ray pattern of pure zirconia reveals a well-crystallized monoclinic phase with a few percentages of tetragonal phases. The monoclinic phase lines are located at  $2\theta = 28.16^\circ$ ,  $31.44^\circ$  and that for tetragonal phase line at  $2\theta = 30.15^\circ$ . The monoclinic CoSZ phase for the prepared catalyst wasn't changed during the addition of Cobalt group. We found that the presence of cobalt oxide enhances the tetragonal structure of zirconia up to 10% then decreases. The presence of tetragonal phase can enhance the acidity and catalytic activity.



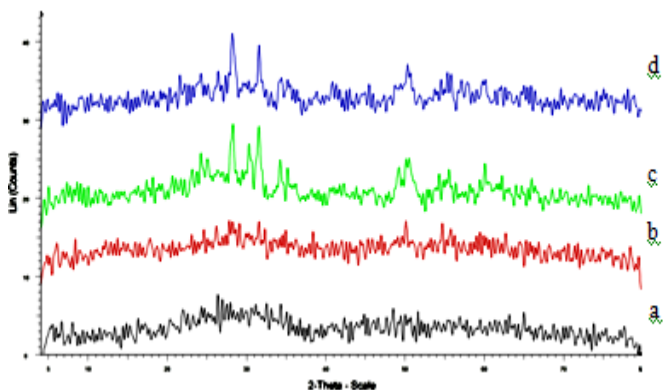
**Figure 1:** X-Ray diffraction patterns of different Co oxide concentration, (a) 5% CoSZ, (b) 10% CoSZ, (c) 15% CoSZ calcined at 600°C

Figure (2) shows that, the samples calcined at 400 °C and 500°C are mainly amorphous. Further increase in calcination temperature higher than 600°C is accompanied by

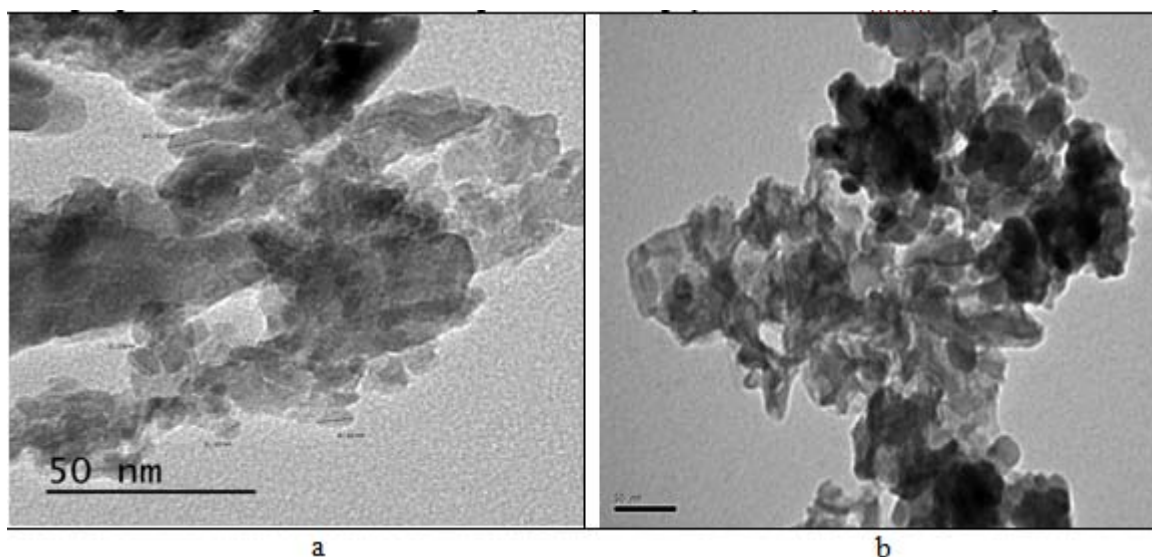
instability of tetragonal phase indicating the sintering of zirconia particles due to the elimination of H<sub>2</sub>O and SO<sub>3</sub>[19]. Also at higher temperatures than 600°C sulphate

decomposes and zirconia undergoes rapid sintering into monoclinic form [27,28]

**Figure 2:** X- Ray diffraction patterns of 10% CoSZ the calcined at different Temperature, (a) 400°C, (b) 500°C, (c) 600°C and (d) 800°C



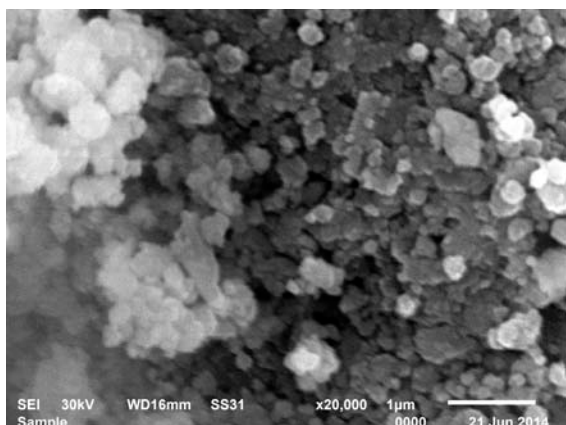
TEM images presented are devoted to help in understanding the correlation between surface structures, which governs the nature of electronic surface state, and the high acid activity exhibited by the CoSZ catalyst [21]. Figure (3) shows that, the presence of cobalt group not only stabilizes the tetragonal ZrO<sub>2</sub> crystallites in the CoSZ samples, but also induces the formation of well faceted particle, i.e., decrease the number of defective termination. It was proposed that the presence of cobalt group near or on these particles could give rise to the highly acidic sites of CoSZ catalyst.



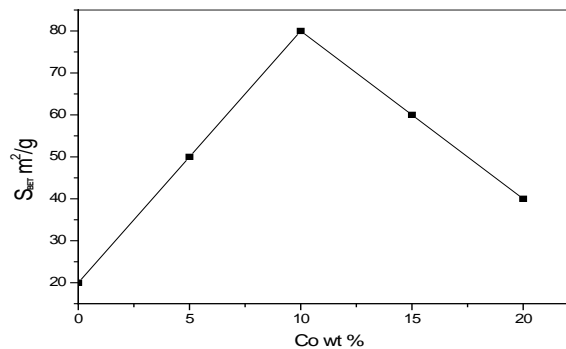
**Figure 3:** TEM image for a) SZ 600 and, b) 10%CoSZ calcined at 600°C

Figure (4) shows a selected SEM micrograph image for 10% CoSZ, For all catalysts irregular edge shaped large particles with variable sizes and forms are obtained. At the microscopic scale, i.e. micrometer range, the surface of most of samples appears to be very porous. Some aggregates formed by very small particles are also present. No significant change in the morphology has been noted after doping variation of cobalt over sulphated zirconia [29]

classification, which is characteristic of slit-shaped pores. The first remark concerning the morphology deals with the surface area of the samples. Figure (5) shows that the surface area increases by increasing the cobalt oxide content upto 10% and then decreases. This indicates that increasing of cobalt oxide content up to 10% stabilizes zirconia against sintering. This increase of cobalt oxide content tends to decrease surface area which can be attributed to blocking the active sites on the surface.



**Figure 4:** SEM image for 10 %CoSZ calcined at 600°C

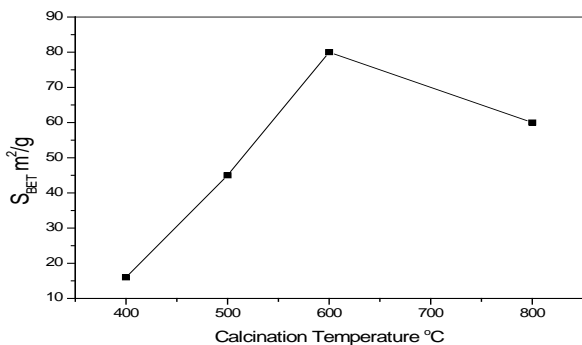


**Figure 5:** Effect of cobalt oxide content on surface area for 10%CoSZ calcined at 600°C

The BET analyses of all the samples give isotherms of type II, with hysteresis loop of type H3 or H4 of the IUPAC

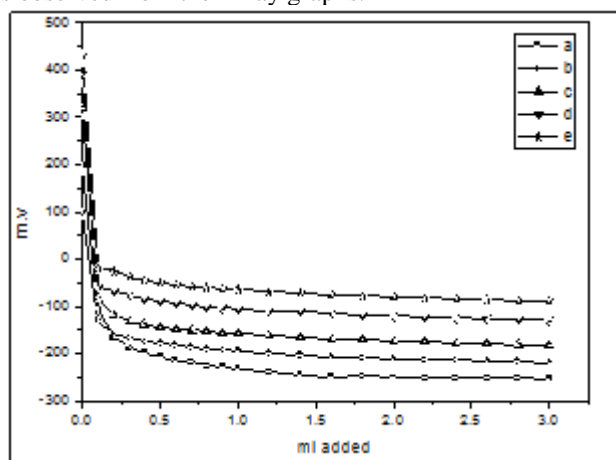
It was found that, the surface area increases by increasing the calcination temperature upto 600 °C and then decreases

as shown in Figure (6), which may be attributed to, by increasing the calcinations temperature show more resistance to sintering process upto 600°C and further increase in calcination temperature, sintering lead to widening of pores and consequently to decrease in the surface area due to the grain growth of the pores. Also increasing the calcinations temperature at 800°C the most of hydroxyl and SO<sub>4</sub> groups have been particularly eliminated from the sample and the pores structure shrinking leading to decrease in surface area. This indicates that, a strong sintering occur in the material, and pore collapse [30]



**Figure 6:** effect of the calcination Temperature on 10% CoSZ

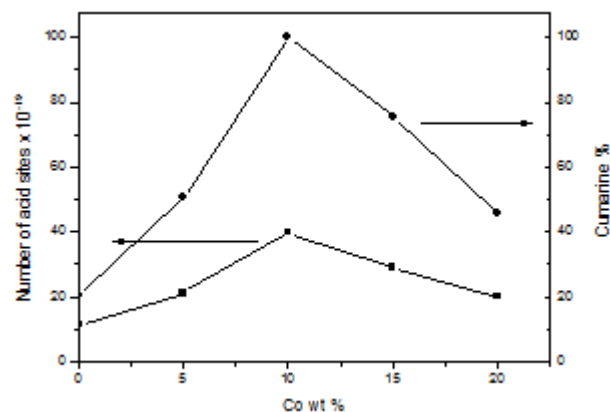
Potentiometric titration with n-butylamine allowed us to measure the maximum acidity of the catalysts [19]. This was determined from the first point of the titration reading, expressed as a measure of the potential acidity as a pH value or in mV as shown in Figures (7). The measured electrode potential is an indicator of the acidic properties of dispersed solid particles. The total numbers of acid sites of the catalysts were affected by cobalt oxide content. The total number of acid sites was increased by increasing the cobalt content upto 10% and then decreased as shown in Figure (8). This may be due to the strong interaction between the cobalt group and sulphated zirconia surface, which is shown in the potentiometric titration and the m.v at zero addition. This can be attributed to the high ratio of tetragonal/ monoclinic as observed from the X-ray graphs.



**Figure 7:** potentiometric titration of n-butylamine in acetonitrile for catalysts calcined at 600°C (a) SZ, (b) 5%CoSZ, (c) 10%CoSZ, (d) 15%CoSZ and (e) 20%CoSZ

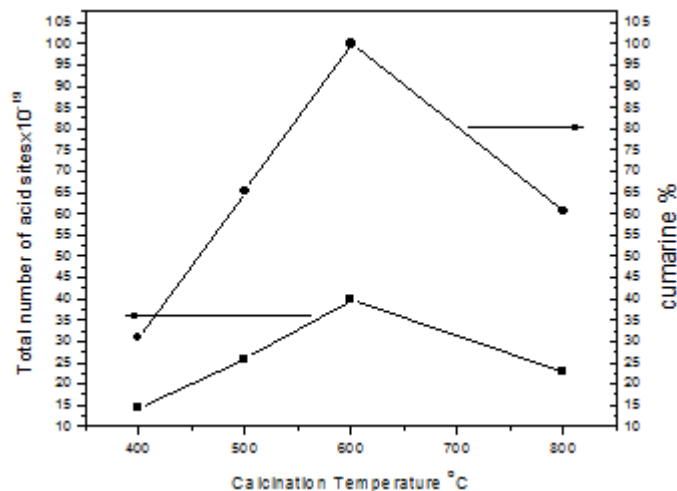
Figure (9) shows the effect of calcinations temperature on the total number of acid sites/g of the investigated catalysts.

The number of acid sites increases by increasing the calcinations temperature upto 600 °C and then decreased. where, the sulphate group bonded to the zirconia surface still attached until the temperature exceed the 600°C, so the sulphate group begin to decompose. By increasing calcination temperature to 800°C, notable decrease in the total acidity can be observed. This may be due to the evolution of SO<sub>3</sub> gas as a result of decomposition of the sulfate groups bonded to the surface of zirconia. Figures (8, 9) show the correlation between number of acid sites and the cumarin % with the variation of the cobalt oxide wt %, and the cumarin % with the calcination temperature respectively. Figure (8) shows that by increasing the cobalt wt % content, the total number of acid sites and cumarin % increases upto 10% and then decreased. By increasing the cobalt contents, the total number of acid sites increase, which increases the coumarine % from 20%, 50%, and 100%.



**Figure 8:** Effect of cobalt oxide content on catalytic activity % and Total Number of acid sites for CoSZ samples calcined at 600°C

Figure (9) shows the effect of calcination temperature on cumarin synthesis by CoSZ samples. It was shown from the figure that the cumarin % increase from 30 % , 65 % and 100% by increasing the calcinations temperature from 400, 500, and 600°C, further increase in calcinations temperature to 800°C, the cumarin % decrease to reach 55%. This may be due to the decomposition of SO<sub>4</sub><sup>2-</sup> and the evolution of SO<sub>3</sub> gas as a result of decomposition of the sulfate groups bonded to the surface of zirconia.



**Figure 9:** Effect of Calcination Temperature on coumarine % and Total number of acid sites for 10% CoSZ samples

#### 4. Conclusion

On the basis of the above finding, the following are the main points that can be summarized: The increase in cobalt concentration in zirconia samples, the tetragonal phase increases by increasing the concentration upto 10%. Further increase in cobalt content enhancement transformation of the tetragonal phase to the monoclinic phase. The increase in cobalt concentration leads to a continuous increase of  $S_{BET}$  upto 10%. Further increase of cobalt 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. CoSZ interaction as well as the calcination temperatures will be responsible for acidity. As the rise of Co oxide content the acidity increases. Also as calcination temperature increases the acidity increases up to 600 °C and then decreases. This due to above 600 °C the  $SO_4^{2-}$  decompose and went as  $SO_x$ . The increase of surface acidity was associated with an increase of cumarin conversion up to 600 °C and then decreased, the catalytic activity was strongly influenced with the textural properties and surface acidities of the catalysts investigated.

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