



# Synthesis, Characterization of Highly Efficient $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ Solid Acid Catalyst and Activity Studies of 2, 4, 5-triaryl imidazoles

Shaikh Sharekh

Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad Sub-Campus, Osmanabad, MS, INDIA

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## Abstract

$\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  solid acid catalyst has been synthesized by coprecipitation followed by impregnation method. Zirconyl oxychloride and ceric ammonium nitrate is used as zirconia and ceria precursor respectively, ammonia is used as precipitating agent and chlorosulfonic acid is used as sulphating agent. The structure characterization of this solid acid catalyst has been studied by FT-IR, XRD, and TGA-DSC. Synthesized solid acid catalyst is employ for preparation of 2,4,5-trisubstituted imidazoles via three-component reactions of benzoin, aldehydes and ammonium acetate under mild conditions. The desired products were formed in high to moderate yields.

**Keywords:** Sulfated ceria-zirconia, 2, 4, 5-triaryl imidazoles, XRD, FT-IR and TGA-DSC.

## Introduction

Solid acids and super acids are the topics of organic synthesis and transformations. Now days, Multicomponent reactions (MCR) are attracting much attention and is of great interest since these reactions allowing the reaction of more than two or three starting materials in one-flask process<sup>1-3</sup>. If these MCRs are combined with heterogenous catalysts which can be recycled, can give the green touch to these reactions. In charge to Solve such trouble, sulfated zirconia solid acid catalysts are used for organic synthesis<sup>4,5</sup>. Here we describe a synthesis of sulfated ceria-zirconia catalyst and its activity as synthesis of 2, 4, 5-triaryl-1H-imidazoles through aldehyde, benzoin and ammonium acetate (scheme-1). A series of homogeneous, heterogeneous catalysts and other methodologies have been effective for synthesis of 2, 4, 5-triaryl-1H-imidazoles<sup>6-16</sup>.

One of Interesting object is that imidazole-containing compound are used in biological activities and synthetic chemistry. Imidazole have many utility in pharmacological and biochemical development<sup>17,18</sup>. For example, the amino acid histidine, the hypnotic agent etomidate<sup>19</sup>, the proton push inhibitor omeprazole<sup>20</sup>, the fungicide ketoconazole<sup>21</sup> and the benzodiazepine antagonist flumazenil<sup>22</sup> are imidazole derivatives. For all above application, the synthesis of imidazoles has become very vital objective in present duration. 2, 4, 5-triaryl-1H-imidazole is harmful towards human life also for animal because it reduces platelet aggregation in some animal class and humans.

In this study, we prepared sulphate promoted ceria-zirconia catalyst by co-precipitation followed by impregnation method. Prepared catalyst has been characterized by XRD, FT-IR and TGA-DSC. Equipped catalyst productively working for the synthesis of 2, 4, 5-triaryl-1H-imidazoles.

## Material and Methods

**Method for preparation of catalyst:** The  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst was prepared by a homogeneous co-precipitation method. For this purpose, requisite quantities of zirconium oxychloride and ceric ammonium nitrate were taken and dissolved separately in deionized water. These resultant mixtures were precipitate with ammonia with dynamic stirring and maintain pH of the solution up to 8-9. At this pH, a yellow precipitate was produced and the precipitate was authorized to resolve for 12 Hours. The following precipitate was filtered off and washed sometimes with deionized water and dried at 110°C for 12 hrs. The powder was crushed and oven-dried. This dried powder was deep in 0.5M chlorosulphonic acid (in dichloroethane). The overload dichloroethane was evaporated by heating on hot plate. The resultant catalyst was oven-dried at 110 °C for 12 h, calcined at 650 °C for 4hrs.

## Results and Discussion

The crystal phase can be determined by X-ray diffraction method. The peak observed in XRD was recognized by using JCPDS data files. The type and amount of acid sites present in the samples relative to one another were studied by the FTIR. The TGA/DSC analysis was carried for determining the calcination temperature.

**X-Ray diffraction Studies:** The X-ray powder diffraction study of sulfate promoted ceria-zirconia catalyst calcined at 650°C is shown in figure 1. As can be noted from this, prepared catalyst shown zirconium cerium oxide ( $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ) was found to be tetragonal primitive (which having the lattice  $a=3.641$ ,  $c=5.244$  and  $\alpha=\beta=\gamma$  which was confirm by JCPDS data having card no. 80-0785) along with formation tetragonal zirconia. Formation ceric sulphate or zirconium sulphate will not observed.

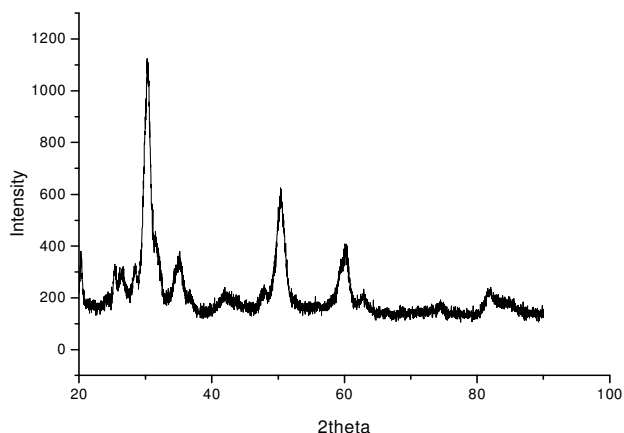


Figure-1

**XRD pattern of Sulfate Promoted Ceria-Zirconia Catalyst**

**FT-IR Studies:** The FT-IR spectrum of sulfate promoted ceria-zirconia catalyst shown in figure 2. The peak at  $1634\text{ cm}^{-1}$  attributed to vibration of OH group<sup>23</sup>. The peak in the area of  $900\text{--}1250\text{ cm}^{-1}$  which may be due to combination of several peaks, which are characteristic of co-ordinated to metal cation and stretching frequencies of S=O and S-O bonds<sup>24</sup>. The bands centered at  $\sim 1600\text{ cm}^{-1}$  and  $\sim 1360\text{ cm}^{-1}$  may be due to Brönsted acid sites. The band at  $\sim 780\text{ cm}^{-1}$  shows characteristics crystalline zirconia.

**TGA – DSC:** TGA is used to pointed best high temperature for calcination of  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  samples, so it is clear that  $600\text{--}650\text{ }^\circ\text{C}$  in this region no sulfate loss is observe. The TGA–DSC plots for the sulfate promoted ceria-zirconia catalyst before calcinations are shown in Fig. 3. There are two stages in the TGA graph. The Stage first was located below  $150\text{ }^\circ\text{C}$  and

which is fear with a strong endothermic peak centred at  $\sim 80\text{ }^\circ\text{C}$ . The above weight loss is due to the removal of the adsorbed water on the surface. Second stage of weight loss is among  $150\text{ }^\circ\text{C}$  and  $\sim 500\text{ }^\circ\text{C}$  corresponding to the elimination of terminal hydroxyl groups bonded to the surface of zirconia-ceria. There is also one of peak in the sort of  $420\text{--}830\text{ }^\circ\text{C}$  observe. In this area there is denial weight defeat is experiential in the TGA curve and thus the exothermic peaks may be credited to move from one stage to another stage i.e. Amorphous phase to a tetragonal metastable phase of zirconia.

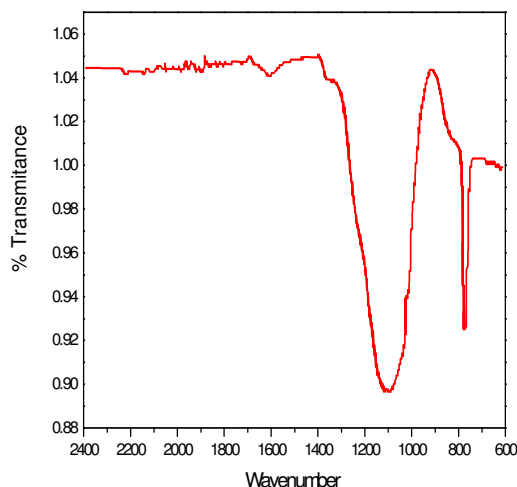


Figure-2

**FT-IR of Sulfate Promoted Ceria-Zirconia Catalyst**

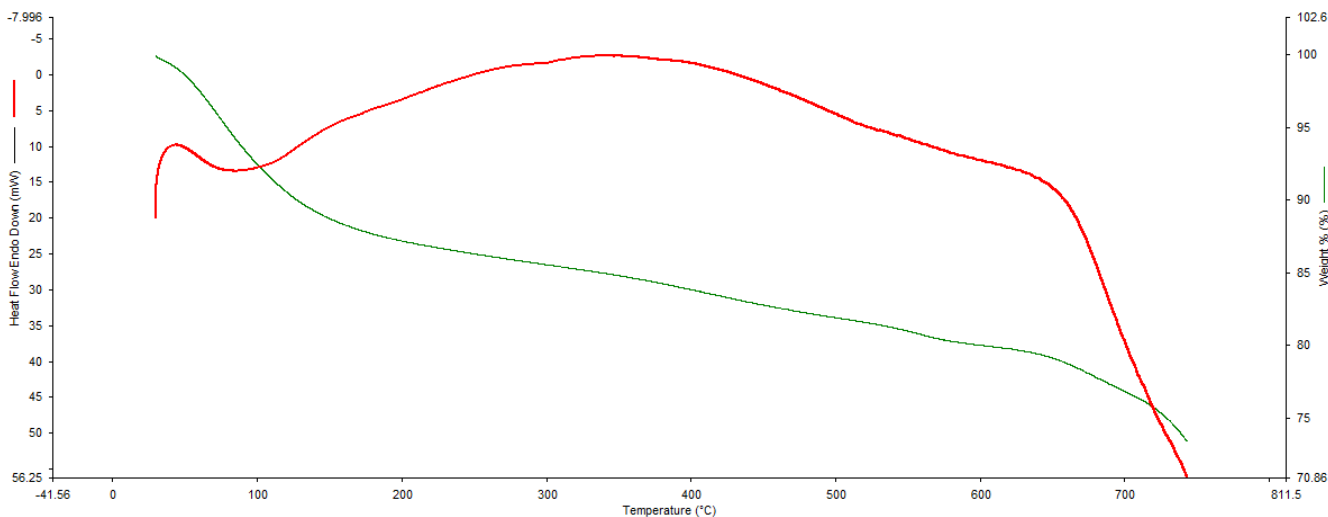


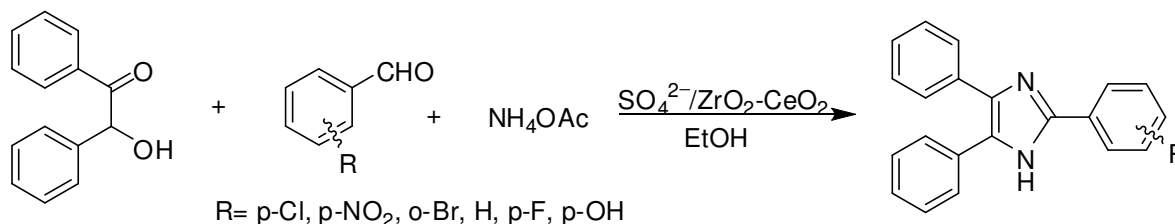
Figure-3

**TGA – DSC of Sulfate Promoted Ceria-Zirconia Catalyst**

**Activity studies:** Production of 2, 4, 5-triaryl-1*H*-imidazoles is received out by experiment,  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  was dispersed in a combination of aldehyde (1mmol), benzoin (1mmol), and ammonium acetate (2.5mmol) and 5ml ethanol in a 25-mL round bottom flask. The content was stirred vigorously at 60°C. The improvement of the reaction was checked by Thin layer chromatography. At the final, the reaction mixture was cooled to room temperature. It was collected by filtration, washed with water, dried and residue crystallized by ethanol to afford the analogous 2, 4, 5-triaryl-1*H*-imidazoles. All the products were known and were identified by comparison of their melting point and  $^1\text{H}$  NMR.

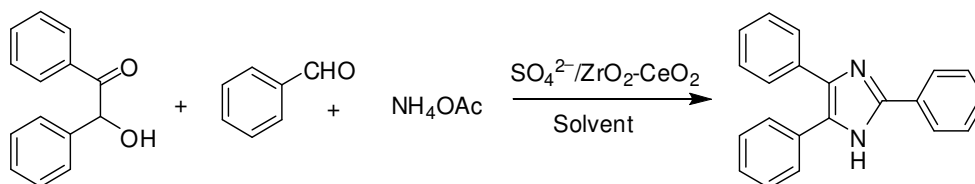
The  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  solid acid catalyst was used for synthesis of 2, 4, 5-triaryl-1*H*-imidazoles by multi component reaction (MCR) between aldehyde, benzoin, and ammonium acetate. For the screening of reaction condition, we used different solvent for multicomponent reaction among

benzaldehyde, benzoin, and ammonium acetate in attendance of  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  solid acid catalyst. Also, we studied the reaction without catalyst and ethanol as solvent. The results are collected in table 1. Various solvents are used out of that ethanol is best solvent at 60 °C for this methodology (table 1, Entry 2) as compare to other solvents such as methanol, THF, acetonitrile and toluene under refluxed condition (table 1, Entry 4-7). By taking these conditions in hand we extended this MCR for various aromatic aldehydes having electron withdrawing as well as donating groups for formation of 2, 4, 5-triaryl-1*H*-imidazoles. The product formed in good to better yield for variety of substrates (table 2, Entry 1-6). The catalyst is easy to handle and purified, through simple filtration. Catalyst recovered and recycle is one of the green aspects. After reaction catalyst be easily split by simple filtration from the reaction combination. The catalyst separate from reaction also used for few more reaction.



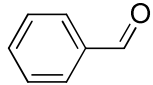
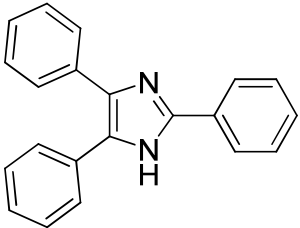
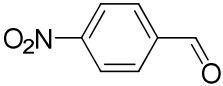
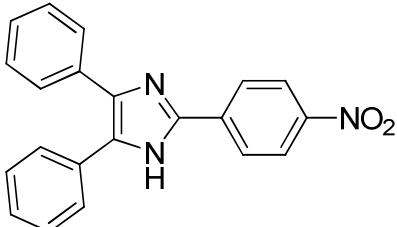
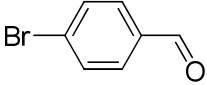
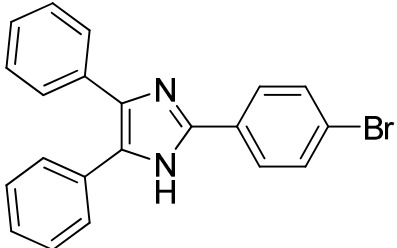
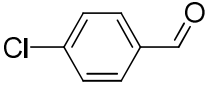
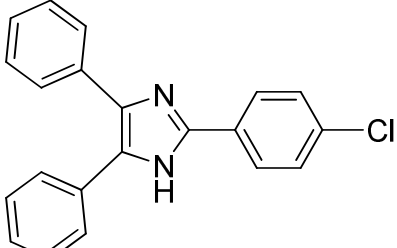
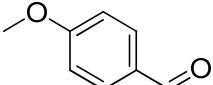
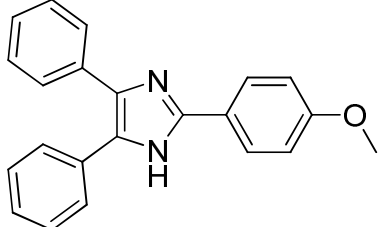
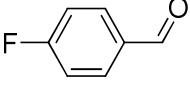
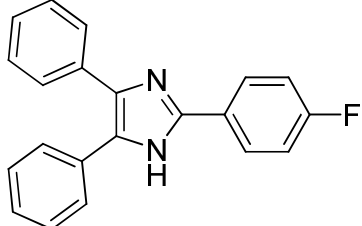
**Scheme-1**  
**Synthesis of trisubstituted-1*H*-imidazoles by using catalyst**

**Table-1**  
**Different Solvent and temperature situation study for synthesis of 2, 4, 5-triaryl-1*H*-imidazoles by Using catalyst**



Entry	Catalyst	Solvent	Temperature(°C)	Yield (%)
1	Nil	Ethanol	R.T.	Nil
2	$\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$	Ethanol	R.T.	Nil
3	$\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$	Ethanol	60	85
4	$\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$	Methanol	75	40
5	$\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$	THF	70	20
6	$\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$	Acetonitrile	80	50

**Table-2**  
**Alternative aromatic aldehyde used for the synthesis of 2, 4, 5-triaryl-1H-imidazoles.**

Entry	Aldehyde	Product	Time (in Hr)	Yield (%)	M.P. (°C)	References
1			3	85	277	[25]
2			3	80	200	[25]
3			3	70	260	[26]
4			3	82	260	[25]
5			3	81	229	[26]
6			3	78	190	[25]

Synthesized product were characterized with  $^1\text{H}$  NMR: 2, 4, 5-Triphenyl-1H-imidazole:  $^1\text{H}$  NMR (400 MHz, DMSO,  $\delta$  ppm): 7.55–7.68 (m, 6H), 7.72–7.75 (m, 3H), 7.9–7.95 (m, 6H), 8.8 (bs, 1H); MS (EI, 70 eV):  $m/z = 297[\text{M}+\text{H}]^+$ .

2-(4-chlorophenyl)-4, 5-diphenyl-1H-imidazole:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.4$ – $7.60$  (m, 6H),  $7.67$ – $7.70$  (m, 2H),  $7.93$ – $8.0$  (m, 6H),  $8.71$  (bs, 1H); MS (EI, 70 eV):  $m/z = 330 [\text{M} + \text{H}]^+$ .

## Conclusion

In termination it is very simple method to prepare  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  solid acid catalyst. The way used for catalyst preparation is coprecipitation process followed by impregnation with chlorosulfonic acid. The depiction of the synthesized catalyst was approved out using various techniques with X-ray diffraction, FT-IR and TGA-DSC. The powder XRD result reveals the formation of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and tetragonal zirconia. FT-IR gives the information about acid sites and interaction of sulfate with metal ions. The synthesized  $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$  catalyst efficiently catalyze the reaction between benzoin, aromatic aldehyde and ammonium acetate using ethanol as solvent under refluxed condition. Mild reaction temperature, high to moderate give up of products and short spanned reaction period are some of the reimbursements connected with this set of rules.

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