

Sulfated $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid acid catalyst for solvent free synthesis of coumarins

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Abstract

A novel $\text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalyst has been employed for Pechmann condensation of phenols under solvent-free conditions. Catalyst loads as low as 10 wt.% could be used leading to high yields with activated phenols at an oil bath temperature of 393 K. To make the catalyst, Ce–Zr–hydroxide gel was prepared by a coprecipitation method and SO_4^{2-} ions were deposited by treating the gel with sulfuric acid and calcined at 923 K. Surface and bulk properties of the catalyst was investigated by means of X-ray powder diffraction, ammonia-temperature programmed desorption, Raman spectroscopy, and BET surface area methods. Characterization results reveal the super acidic nature of the catalyst. The methodology presented offers significant improvements for the synthesis of coumarins with regard to yield of products, simplicity in operation, and green aspects by avoiding toxic conventional catalysts and solvents.

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1. Introduction

Coumarins have been extensively investigated and widely used but still generate much interest. Coumarins are structural units of several natural products and feature widely in pharmacologically and biologically active compounds [1,2]. Many coumarins and coumarin derivatives exhibit high level of biological activity [3]. Besides functionalized coumarins [3–7], polycyclic coumarins such as calanolides [8], isolated from *Calophyllum* genus, and others have shown potent anti-HIV (NNRTI) activity.

Coumarins have been synthesized by several routes including Pechmann [9], Perkin [10], Knoevenagel [11], Reformatsky [12] and Wittig reactions [13], and by flash vacuum pyrolysis [14]. A highly useful method for the synthesis of coumarins is the Pechmann reaction, which starts from phenols. In the conventional production of coumarins by the Pechmann reaction, concentrated sulfuric acid is used as the catalyst [15]. This process causes formation of byproducts, requires long reaction

times, and encompasses corrosion problems [16]. For these reasons, there have been several attempts in the literature to find alternative and environmentally benign synthesis routes. Various catalyst systems such as Nafion-H [17], zeolite H-BEA, Amberlyst 15 [18], montmorillonite clay [19], ionic liquids [20], and W/ZrO_2 solid acid [21], have been employed for this purpose. Some organic acids and metal Lewis acids have also been examined for this condensation reaction [22]. Although these methods are suitable for certain synthetic conditions, however, many of these procedures are associated with one or more disadvantages such as expensive reagents, long reaction times, tedious work-up procedure, low selectivity, and large amounts of catalysts which would eventually result in the generation of large amounts of toxic waste.

In continuation to our quest in organic synthesis under solvent-free conditions employing solid catalysts [23], we report here an efficient method for the preparation of coumarins using a novel $\text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ composite solid acid catalyst in the Pechmann reaction of a neat mixture of a phenol and a β -keto ester. Catalyst loads as low as 10 wt.% (to that of phenols) could be used leading to good to high yields with activated phenols at a moderate temperature of 393 K within a short period of time. The acidic $\text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalyst was synthesized by making Ce–Zr–hydroxide gel by a homogenous

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coprecipitation method and impregnating with sulfate ions. The prepared catalyst was characterized by means of BET surface area, X-ray diffraction (XRD), Raman spectroscopy (RS), and NH_3 -temperature programmed desorption (TPD) techniques and was evaluated for the synthesis of coumarins at 393 K under solvent free conditions in the liquid phase. As presented, this methodology offers significant improvements with regard to yield of products, simplicity in operation, and green aspects by avoiding toxic catalysts and solvents.

2. Experimental

2.1. Catalyst preparation

The $\text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalyst was prepared by adopting a two-step procedure. Ceria–zirconia hydroxide gel was prepared first by a coprecipitation method and then impregnated with sulfate ions. To make $\text{Ce}(\text{OH})_4\text{--Zr}(\text{OH})_4$ (1:1 mole ratio based on oxides), a mixture solution of ammonium cerium nitrate $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}]$ and zirconium nitrate $[\text{Zr}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}]$ were hydrolysed with dilute aqueous ammonia solution (pH 8) under vigorous stirring. Thus, obtained precipitate was filtered, washed and then dried at 383 K for 12 h. The obtained hydroxide gel was sulfated by adding a measured volume of 0.5 M H_2SO_4 solution, so as to reach the equivalence of 5 mL of pure H_2SO_4 per gram of $\text{Ce}(\text{OH})_4\text{--Zr}(\text{OH})_4$ gel. This process was performed under mechanical stirring and maintained for 1 h, subsequently dried at 393 K for 3 h and calcined at 923 K for 4 h. The finished catalyst stored in vacuum desiccator and was activated at 523 K for 5 h in vacuum before catalytic runs.

2.2. Catalyst characterization

The BET surface area was measured by N_2 adsorption at liquid N_2 temperature using a Micromeritics Gemini 2360 instrument. Powder X-ray diffraction patterns were recorded on a Siemens D-5000 diffractometer, using Ni-filtered $\text{Cu K}\alpha$ (0.15418 nm) radiation source. Crystalline phases were identified by comparison with the reference data from International Center for Diffraction Data (ICDD) files. The NH_3 -temperature programmed desorption measurements were carried out on an Autochem 2910 instrument (Micromeritics, USA), in the temperature range 373–873 K at 10 K min^{-1} ramp. A thermal conductivity detector was used for continuous monitoring of the desorbed ammonia and the areas under the peaks were integrated using GRAMS/32 software. Prior to TPD studies, the sample was pretreated at 473 K for 1 h in a flow of ultra pure He gas (40 mL min^{-1}). After pretreatment, the sample was saturated with 10% ultra pure anhydrous ammonia gas (balance He; 75 mL min^{-1}) at 353 K for 2 h and subsequently flushed with He (60 mL min^{-1}) at 373 K for 2 h to remove the physisorbed ammonia.

2.3. Activity studies

In a typical experiment, $\text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ (10 wt.% to that of phenols) was dispersed in a mixture of phenols (4.54 mmol)

and methyl acetoacetate/ethyl acetoacetate (6.80 mmol) in a 25-mL batch reactor equipped with a distillation condenser. The content was stirred vigorously at 393 K. The progress of the reaction was monitored by TLC. At the end of the reaction, the reaction mixture was treated with acetone and filtered to recover the catalyst. The wet catalyst was washed with dichloromethane and recycled to check the reusability of the catalyst. No appreciable change in the reactivity was observed for the successive 2–3 runs. The filtrate was evaporated under reduced pressure to obtain the crude product. Thus obtained product was washed with water, filtered and dried at 373 K. The product was purified by dissolving in 20 mL 1 M NaOH and then regenerated with 10 mL 2 M H_2SO_4 solution. The purified products were characterized by melting point, ^1H NMR and mass spectroscopy methods.

3. Results and discussion

It is an established fact in the literature that Pechmann reaction proceeds through transesterification and intramolecular hydroxyalkylation, followed by dehydration [18,24]. These three steps are all typical acid-catalyzed reactions. Therefore, the outcome of the Pechmann reaction depends very much on the Brønsted acidity of the catalysts [16]. Recently, zirconia-based solid acids have emerged as attractive alternative catalysts in terms of their acidic strength and environmentally benign character for various reactions that are catalyzed by toxic and corrosive Lewis acids and expensive ionic liquids [23,25]. Incorporation of zirconium cations into the ceria unit cell or vice versa modifies the surface acid–base sites, as the exposed Ce^{4+} and Zr^{4+} ions act as Lewis acid sites and O^{2-} ions as Brønsted or Lewis base sites [26]. The acid strength of the mixed oxide varies depending on the charge to radius ratio of the cations. The Zr^{4+} ion has an ionic radius of 0.84 \AA , which is smaller than that of Ce^{4+} (0.97 \AA) and is expected to generate strong acid sites in the solid solutions [27]. Further, surface hydroxyl groups could be generated due to dissociative adsorption of water on the highly polar $\text{M}_1\text{--O--M}_2$ bonds. In this context, we were interested to investigate the effect of sulfation on the physicochemical characteristics of the $\text{CeO}_2\text{--ZrO}_2$ composite oxide solid solutions, and to explore their acidic properties for various useful catalytic reactions.

The BET surface area of the catalyst calcined at 923 K was found to be $126 \text{ m}^2 \text{ g}^{-1}$ which is reasonably high indicating porous nature of the sample. The powder X-ray diffraction pattern of the sample is shown in Fig. 1. Close inspection of the XRD pattern reveals formation of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid solution and zirconium sulfates. A tetragonal $\text{Ce}_{0.16}\text{Zr}_{0.84}\text{O}_2$ (PDF-ICDD 38-1437) phase could be identified and the lines due to different type of surface zirconium sulfates namely, zirconium sulfate hydroxide $[\text{Zr}(\text{OH})_2\text{SO}_4]$ (PDF-ICDD 26-1001) and zircosulfate $[\text{Zr}(\text{SO}_4)_2]$ (PDF-ICDD 08-0495) could be manifested. No XRD lines pertaining to cerium sulfate compounds are observed. Similar findings were reported by Gao et al. [28], who synthesized $\text{SO}_4^{2-}/\text{CeO}_2$ sample by macerating ceria nanoparticles in sulfuric acid solution and obtained CeO_2 particles with strongly bonded SO_4^{2-} groups on the surface. As can be noted fur-

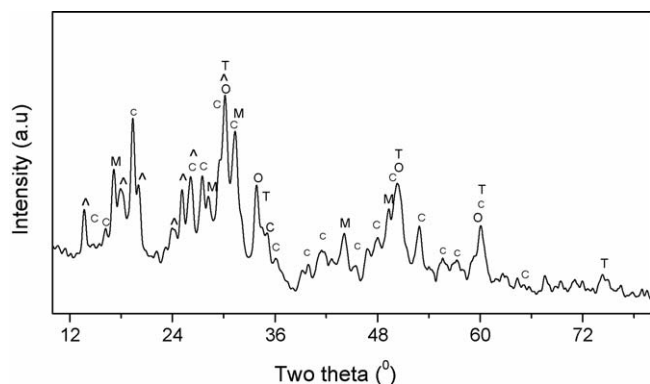


Fig. 1. XRD patterns of $\text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ sample calcined at 923 K. Peak legends is as follows: (O) lines due to $\text{Ce}_{0.16}\text{Zr}_{0.84}\text{O}_2$; (C) lines due to $\text{Zr}(\text{OH})_2\text{SO}_4$; (·) lines due to $\text{Zr}(\text{SO}_4)_2$; (T) lines due to $t\text{-ZrO}_2$; (M) lines due to $m\text{-ZrO}_2$.

ther from the XRD patterns that both tetragonal and monoclinic phases of zirconia are present and the former have gained more in intensity. Fig. 2 represents Raman spectra of the sample calcined at 923 K. As can be noted from this figure, all zirconia related bands become obvious indicating a very strong interaction of surface sulfate species with zirconia portion of the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ composite oxide. The typical Raman bands due to tetragonal ZrO_2 are observed in the $150\text{--}700\text{ cm}^{-1}$ region. Strong bands at 268 , ~ 460 and 648 cm^{-1} together with a shoulder at 605 cm^{-1} and smaller features around 312 , 382 and 560 cm^{-1} are indicative for the tetragonal modification of the zirconia. A sharp doublet observed at 178 and 189 cm^{-1} along with a sharp peak at 473 cm^{-1} are indicative for the presence of monoclinic zirconia [29]. The RS peaks pertaining to tetragonal and monoclinic modifications are in agreement with the XRD measurements. Further, the RS bands due to surface sulfates are visible in the range $1000\text{--}1100\text{ cm}^{-1}$. The presence of bands in the $\text{Zr}\text{--}\text{O}\text{--}\text{S}$ stretching region at 1017 , 1050 and 1032 cm^{-1} indicate the existence of more than one type of surface sulfate species [30], in line with XRD analysis [31], and support the formation of $[\text{Zr}(\text{OH})_2\text{SO}_4]$ and $[\text{Zr}(\text{SO}_4)_2]$. The bands observed at 1068 and 1079 cm^{-1} could be tentatively assigned to stretching mode of the surface sulfate groups connected to Ce. On the whole Raman spectroscopy study reveals the formation of surface sulfates formed due to the preferential interaction of the

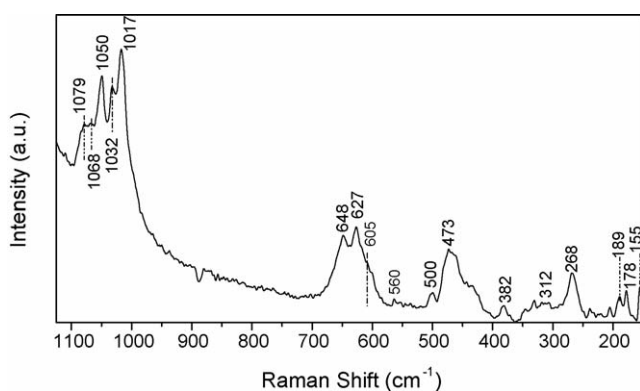


Fig. 2. Raman spectrum of $\text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ sample calcined at 923 K.

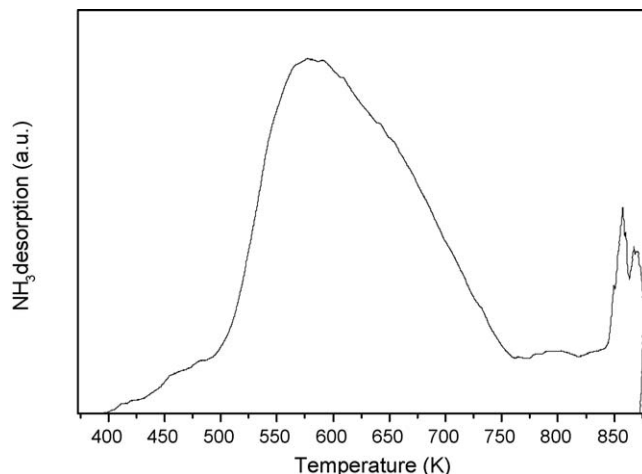


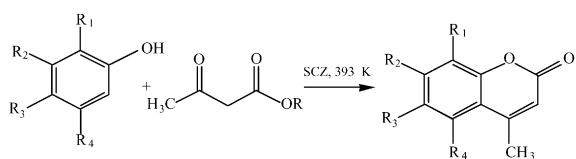
Fig. 3. Ammonia-TPD profile of $\text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ sample calcined at 923 K.

sulfate promoter with the zirconia portion of the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ composite oxide.

The NH_3 -TPD profile of the sample is shown in Fig. 3. Sulfate groups can generate strong acidity, when adsorbed on the oxide supports [23,25]. Sulfate species themselves are Lewis acids or by attracting electrons they generate Lewis acid centers on the oxide surfaces. These Lewis acid sites increase the Brønsted acid strength of the surface hydroxyl groups present on the surfaces [25]. Further, the chemical states of the sulfate groups sometimes determine the acidity of the oxide surfaces. Calcination at higher temperatures leads to changes in ionic to covalent character with $\text{S}=\text{O}$ bond order close to 2, which is responsible for generating strong acidic active centers on the oxide surfaces. A broad ammonia desorption profile in the $500\text{--}750\text{ K}$ range with highest desorption around 580 K could be noted. This broad peak can be considered as an indication for the presence of high concentration of acid sites with moderate strength. In addition to this broad peak, two high temperature desorption peaks are also observed at 857 and 870 K , respectively. The formation of superacid sites could be responsible for the observation of these high temperature desorption peaks in agreement with literature reports [32]. The position of ammonia desorption peak corresponding to the super-acidic sites is influenced by the nature of the mixed oxide with zirconia. In the case of sulfated alumina–zirconia and sulfated titania–zirconia samples a single high temperature desorption peak was observed at about 873 K [33,34]. However, in the present case two close peaks at 857 and 870 K are noted. These observed high temperature peaks represent two different types of superacid sites with slightly differing their acidity.

The sulfated $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid superacid catalyst was evaluated for liquid phase synthesis of coumarins in solvent free conditions and summarized in Table 1. For all these reactions the weight of the catalyst with respect to phenols was fixed at 10 wt.%. For entries 1–4 in Table 1, ethyl acetoacetate, and for entries 5–8 the reaction was carried out with methyl acetoacetate. Reactions of 1,3,5-trihydroxybenzene with ethyl acetoacetate and methyl acetoacetate (entries 4 and 8) took place very fast within 4 and 5 min, respectively. This is mainly due to the

Table 1
 $\text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalyzed Pechmann condensation in solvent free conditions



| Entry | Phenols | β -Ketoester | Time (min) | Yield (%) |
|-------|-------------------------------|---------------------|------------|-----------|
| 1 | 1,3-Dihydroxybenzene | Ethyl acetoacetate | 143 | 87 |
| 2 | 1,3-Dihydroxy-5-methylbenzene | Ethyl acetoacetate | 60 | 84 |
| 3 | 1,2,3-Trihydroxybenzene | Ethyl acetoacetate | 25 | 80 |
| 4 | 1,3,5-Trihydroxybenzene | Ethyl acetoacetate | 4 | 94 |
| 5 | 1,3-Dihydroxybenzene | Methyl acetoacetate | 77 | 94 |
| 6 | 1,3-Dihydroxy-5-methylbenzene | Methyl acetoacetate | 40 | 93 |
| 7 | 1,2,3-Trihydroxybenzene | Methyl acetoacetate | 15 | 93 |
| 8 | 1,3,5-Trihydroxybenzene | Methyl acetoacetate | 5 | 77 |

Table 2
 Activities of various catalysts for the reaction of 1,2,3-trihydroxybenzene with ethyl acetoacetate

| Entry | Catalyst | Time (min) | Yield (%) | Reference |
|-------|--|------------|-----------|--------------|
| 1 | $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ | 04 | 94 | Present work |
| 2 | $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ | 20 | 92 | [35] |
| 3 | ZrCl_4 | 05 | 93 | [36] |
| 4 | [bmim]PF ₆ ionic liquid | 45 | 95 | [37] |
| 5 | Wells–Dawson heteropolyacid ($\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 24\text{H}_2\text{O}$) ^a | 300 | 78 | [38] |
| 6 | Wells–Dawson heteropolyacid ($\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 24\text{H}_2\text{O}$) ^b | 48 | 97 | [38] |
| 7 | W–ZrO ₂ | 300 | 56 | [22] |

^a Toluene as solvent.

^b Solvent free condition.

presence of three hydroxyl groups that cooperate in activating the aromatic ring for hydroxyalkylation. Similarly, reactions of 1,2,3-trihydroxybenzene with ethyl acetoacetate and methyl acetoacetate (entries 3 and 7) took place in 25 and 15 min, respectively, which are slower than that of the reactions of 1,3,5-trihydroxybenzene presumably due to steric hindrance of hydroxyl groups. The reactions of 1,3-dihydroxybenzene with ethyl acetoacetate and methyl acetoacetate (entries 1 and 5) occurred within 143 and 77 min, respectively. This could be due to the presence of only two hydroxyl groups, which are meta to each other. However, in the case of 1,3-dihydroxy-5-methylbenzene, the reactions (entries 2 and 6) were somewhat faster than that of the reactions of 1,3-dihydroxybenzene that could be due to the presence of methyl group ortho to the position of hydroxyalkylation.

To study the influence of catalyst amount on the yield of reaction product and time of reaction, the amount of catalyst was varied in the case of highest time taking reaction that is the reaction between 1,3-dihydroxybenzene and ethyl acetoacetate (entry 1, Table 1). When the amount of catalyst was doubled i.e. 20 wt.% with respect to 1,3-dihydroxybenzene, substantial reduction in the reaction time was observed. The reaction occurred in 110 min only giving 92% yield as compared to 147 min in the earlier case.

Table 2 compares the activities of various catalysts studied in the open literature for the reaction of 1,3,5-trihydroxybenzene with ethyl acetoacetate (entry 4, Table 1) [22,35–38]. Interest-

ingly, on the sulfated $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalyst a 94% yield was obtained in just 4 min. The Table 2 clearly signifies the usefulness of the present catalyst for the synthesis of coumarins. The presence of high concentration of strong Brønsted acid sites along with Lewis acid sites in the catalyst are primarily responsible for rapid reactions leading to high yields of the products.

4. Conclusions

A novel $\text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid acid catalyst was synthesized from the uncalcined cerium–zirconium hydroxide gel obtained by a coprecipitation method followed by impregnation with sulfuric acid. The physicochemical characterization of the synthesized catalyst was carried out using various techniques including X-ray diffraction, Raman spectroscopy and ammonia-TPD. The powder XRD and Raman spectroscopic results revealed a strong interaction of the sulfate ions with zirconia portion of the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ composite oxide leading to the formation of surface sulfates, accompanied by the formation of a tetragonal $\text{Ce}_{0.16}\text{Zr}_{0.84}\text{O}_2$ phase. The ammonia-TPD experiments revealed that sulfated $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ leads to the formation of super-acidic sites in the catalyst. The synthesized $\text{SO}_4^{2-}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalyst was found to efficiently catalyze the Pechmann reaction at 393 K. Mild reaction temperature under solvent free conditions, high yield of products, and shorter reaction times are some of the advantages associated with this

protocol. The pronounced advantage of this novel catalytic system is expected to contribute to the development of more benign Pechmann condensation of phenols with methyl acetoacetate and ethyl acetoacetate.

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