Heterogeneously Catalyzed Pechmann Condensation Employing the Tailored Zn_{0.925}Ti_{0.075}O NPs: Synthesis of Coumarin

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ABSTRACT: A novel heterogeneous catalytic method was developed for the synthesis of coumarin and its derivatives using the Ti(IV)-doped ZnO matrix forming catalyst Zn_{0.925}Ti_{0.075}O having a high surface area and good Lewis acidity. The catalyst shows high activity toward a broad spectrum of the substituted phenols with β-ketoesters such as ethyl acetoacetate, ethyl butyryl acetate, ethyl benzoyl acetate, and so forth in good yields over short reaction times during the synthesis of coumarins. The methodology was further extended for the synthesis of ayapin molecules. The catalyst also shows recycle activity up to seven cycles with very good stability.

INTRODUCTION

Coumarins are a class of oxygen heterocycles, contributing in the field of natural products which are medicinally important.1 Coumarin derivatives are utilized as intermediate chemicals in the synthesis of pharmaceuticals, agrochemicals, insecticides, food additives, fragrances, and cosmetics.2 Additionally, they are applicable as optical whitening agents, laser colors, dyes, and fluorescent probes for the identification of biologically important chemical species as medicinal stains.3 In the synthetic organic chemistry, the class of coumarin compounds is useful for the synthesis of chromones, coumarones, fluoroacoumarins, and 2-acyl resorcinol.4 However, many important drug molecules have coumarin moieties such as warfarin, calanolide A, 667 coumate, novobiocin, ensaculin and so forth. Amongst all, Pechmann reaction is widely useful for the synthesis of coumarin because of the simple starting materials, mild reaction conditions, and excellent yields of the products in short reaction times. Various catalysts such as mineral acids like H_2SO_4, HCl, H_3PO_4, CF_3COOH, HClO_4, ClSO_3H, PTSA, and oxalic acid as well as Lewis acids such as ZnCl_2, FeCl_3, SnCl_4, SnCl_2·H_2O, TiCl_4, AlCl_3, ZrCl_4, InCl_3, BiCl_3, Sm(NO_3)_3, BF_3·H_2O, CAN, Cu(ClO_4)_2, BaCl_2, and NbCl_5 were also reported in the conventional synthesis of coumarin via Pechmann condensation.13 Similarly, different heterogeneous catalysts were also employed for Pechmann condensation such as Al-MCM-41,14 Al-SBA-1 molecular sieves,15 Keggin structures heteropolyacids,16 graphite-montmorillonite K10,17 H_3[NaP_5W_{30}O_{110}O_{10}],18 silica triflate,19 mesoporous zirconium phosphate,20 ZrOCl_2·8H_2O/SiO_2,21 pentfluoro phenyl ammonium triflate,22 periodic mesoporous silica chloride,23 melamine–formaldehyde resin-supported H^+,24 PEG-SO_3H,25 poly(4-vinylpyridinium) hydrogen sulfate,26 PVP-supported phosphotungstic acid,27 poly(4-vinylpyridine)-supported copper iodide,28 1-butyl-3-methylimidazolium chloroaluminate, and 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid.29 Nowadays, scientists are paying considerable attention to the invention of nanomaterial-based catalysts having an extensive range of various textural and microscopy properties. However, controlled synthesis of nanostructures has received enormous attention in the heterogeneous catalysis due to various surface properties of NPs by modifying their composition, size, and shape.30 In recent reports, coumarin and their derivatives were synthesized using various nanocatalysts such as magnetically separable Fe_3O_4@SiO_2@EtSO_3H,31 zirconium(IV)-modified...
silica@magnetic nanocomposites, with various functionalities exerting Bronsted acidity-like CMK-5-supported sulfonic acid, sulfated zirconia, sulfated Ce$_{x}$Zr$_{1-x}$O$_{2}$, WO$_3$—ZrO$_2$ nanocomposites, and 12-tungstophosphoric acid supported onto ZrO$_2$ (12-TPA/ZrO$_2$). Nevertheless, homogeneous-catalyzed methods suffer because of the formation of unnecessary byproducts, long reaction time, the use of stoichiometric reagents/catalysts, and the disposal of waste leading to environmental pollution. Similarly, the drawbacks accompanying with the biphasic catalytic systems are as the use of a toxic and costly catalyst, unsatisfactory yields and harsh reaction conditions, tedious workups, activation of catalyst, and longer reaction time. To overcome from all the aforementioned limitations, there is a scope for the design of an inexpensive, efficient, recyclable, and environmentally benign approach. Goswami had developed the catalytic protocol for Pechmann condensation using ZnO and pyridine dicarboxylic acid together as a dually activated organo- and nanocatalyst of various phenols and β-ketoesters.

In the present research work, we have developed a solid acid catalyst (Zn$_{1-x}$Ti$_x$O NPs) to facilitate Pechmann condensation for the synthesis of coumarin under mild reaction conditions. In the continuation of the coumarin synthesis, ayapins were also synthesized using similar reaction conditions. We have reported the catalyst Zn$_{1-x}$Ti$_x$O NPs for the synthesis of fluorescein via the Friedel-craft’s acylation approach. The textural properties of Zn$_{1-x}$Ti$_x$O NPs show high surface area and Lewis acidity characterized by Brunauer–Emmett–Teller surface area measurements and pyridine Fourier transform infrared spectra. Further, roughly spherical morphology of Zn$_{1-x}$Ti$_x$O NPs was confirmed by scanning electron microscopy.

### RESULTS AND DISCUSSION

#### Catalyst Screening

The catalyst activity was tested in the model reaction for the coumarin synthesis using EAA and phloroglucinol with the prepared catalysts at 110 °C under solvent-free conditions, and the results are presented in Table 1. Initially, in order to verify the role of the catalyst, the reaction was performed without any catalyst for 24 h; no product was obtained (Table 1, entry 1). ZnO showed poor reactivity toward Pechmann condensation and gives traces of the product over 5 h (Table 1, entry 2). After that, Zn$_{1-x}$Ti$_x$O nanoparticles were screened for their activity during the synthesis of coumarin, where Zn$_{0.975}$Ti$_{0.025}$O gave very low yield (37%) of 3a (Table 1, entry 3) due to a low concentration of Ti(IV). Zn$_{0.950}$Ti$_{0.050}$O showed improvement in the performance under the same reaction conditions, with the yield of 3a about 60% (Table 1, entry 4). Zn$_{0.925}$Ti$_{0.075}$O

| entry | catalyst | time (h) | yield (%) | TON/TOF (h) |
|-------|----------|----------|-----------|-------------|
| 1     | no catalyst | 24       | 0/0       |             |
| 2     | ZnO       | 5        | Trace     | 0/0         |
| 3     | Zn$_{0.975}$Ti$_{0.025}$O | 3 | 37 | 270/90 |
| 4     | Zn$_{0.950}$Ti$_{0.050}$O | 4 | 60 | 201/50.44 |
| 5     | Zn$_{0.925}$Ti$_{0.075}$O | 3 | 88 | 203/67.69 |
| 6     | Zn$_{0.900}$Ti$_{0.100}$O | 3 | 88 | 149/49.91 |

*Reaction conditions: EAA (2 mmol), phloroglucinol (2 mmol), catalyst (10 mol %), temp. (110 °C), isolated yields, TON = moles of product/moles of active sites in the catalyst.

#### Solvent Screening

The solvent screening for Pechmann condensation was carried out using EAA and phloroglucinol with the catalyst Zn$_{0.925}$Ti$_{0.075}$O (10 mol %) under reflux conditions (Table 2). The results showed that DCM, ethyl acetate, acetonitrile, and water gave lower yields (Table 2, entries 1-4), while toluene and DMF did not show any product (Table 2, entries 5 and 6). Solvent-free conditions gave the best yield of 88% (Table 2, entry 7). The reaction was also performed at temperatures of 90 and 130 °C, and the yield was 61% and 80%, respectively (Table 2, entries 9 and 10).

| entry | solvent | temp. (°C) | time (h) | yield (%) |
|-------|---------|------------|----------|-----------|
| 1     | DCM     | 40         | 8        | 24        |
| 2     | ethyl acetate | 78 | 8 | 16 |
| 3     | acetonitrile | 80 | 8 | 37 |
| 4     | water   | 100        | 5        | 41        |
| 5     | ethanol | 78         | 5        | 63        |
| 6     | toluene | 110        | 10       | NR        |
| 7     | DMF     | 150        | 10       | NR        |
| 8     | solvent-free | 110 | 3 | 88 |
| 9     | solvent-free | 90 | 5 | 61 |
| 10    | solvent-free | 130 | 3 | 80 |

*Reaction conditions: EAA (2 mmol), phloroglucinol (2 mmol), Zn$_{0.925}$Ti$_{0.075}$O (10 mol %), isolated yields.

Table 1. Catalytic Screening for the Coumarin Synthesis by Pechmann Condensation

Table 2. Solvent Screening for Pechmann Condensation

Figure 1. Drug molecules containing the coumarin motif.
displayed the highest catalytic activity of coumarin and yield 88% (Table 1, entry 5). Further, Zn$_{0.900}$Ti$_{0.100}$O showed no improvement in the yield (88%) of 3a (Table 1, entry 6). Thus, Zn$_{0.925}$Ti$_{0.075}$O is found to be the best catalyst for further optimization studies in the synthesis of coumarin by Pechmann condensation.

**Solvent Screening.** The various solvents were also studied for optimizing the reaction conditions during the synthesis of coumarin, and the results are summarized in Table 2. Aprotic polar solvents such as dichloromethane (DCM) and ethyl acetate gave only 24 and 16% yields of 3a, respectively, after 8 h (Table 2, entry 1 and 2), whereas, in the presence of acetonitrile as a solvent, the yield of the desired product was enhanced to 37% (Table 2, entry 3). The protic polar solvents such as water and ethanol afforded the 41 and 63% yield of desired product 3a, respectively (Table 2, entry 4 and 5). With nonpolar solvents such as toluene as well as high boiling point solvents such as dimethylformamide (DMF), they do not show any conversion even after prolonged reaction times (Table 2, entry 6 and 7). The maximum yield of 3a achieved was 88%, in solvent-free reaction conditions at 110 °C in a very short reaction time of about 3 h (Table 2, entry 8). At a lowered temperature of 90 °C, the yield was reduced to 61% and requires 5 h for the completion of the reaction (Table 2, entry 9). Furthermore, the reaction temperature maintained at 130 °C; unexpectedly, reduction in the yield of 3a was observed under same reaction conditions (Table 2, entry 10). From the above set of observations, it is proved to be solvent-free conditions, and temperature 110 °C was suitable for the synthesis of coumarin (3a) under the optimized reaction conditions.

**Effect of Catalyst Loading.** The effect of catalyst loading was studied by varying the mol % in the reaction with 5, 10, and 15 mol %, and the results are presented in Table 3. Initially, the amount of the Zn$_{0.925}$Ti$_{0.075}$O catalyst was 5 mol %, the yield is 67%, and requires 5 h time for the reaction (Table 3, entry 1). When the catalyst amount was increased to 10 mol %, there is a significant increase in yield of about 88% of 3a (Table 3, entry 2). However, upon increasing the catalyst amount to 15 mol %, there was no further improvement in the yield (88%) of the product (Table 3, entry 3). Thus, 10 mol % Zn$_{0.925}$Ti$_{0.075}$O catalyst was the most optimal for Pechmann condensation of ethyl acetoacetate and phloroglucinol.

**Substrate Scope.** The excellent performance of the catalyst system with 10 mol % Zn$_{0.925}$Ti$_{0.075}$O under solvent-free conditions during the synthesis of coumarin encouraged us to elaborate their applications for a broad substrate scope.

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**Table 4. Substrate Scope for Coumarin Synthesis from Activated Phenols and Various β-Ketoesters Using 10 mol % Zn$_{0.925}$Ti$_{0.075}$O in the Solvent-Free Condition**

| entry | catalyst amount (mol %) | time (h) | yield (%) |
|-------|-------------------------|----------|-----------|
| 1     | 10                      | 3        | 88        |
| 2     | 15                      | 3        | 88        |

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*Reaction conditions—β-ketoesters (2 mmol), phenols (2 mmol), Zn$_{0.925}$Ti$_{0.075}$O (10 mol %), temperature—110 °C, solvent-free, time specified as given, isolated yields*. 

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*Table 3. Effect of Catalyst Concentration in Pechmann Condensation*

![Chemical structure]

| entry | catalyst amount (mol %) | time (h) | yield (%) |
|-------|-------------------------|----------|-----------|
| 1     | 5                       | 5        | 67        |
| 2     | 10                      | 5        | 88        |
| 3     | 15                      | 3        | 88        |

*Reaction conditions—EAA (2 mmol), phloroglucinol (2 mmol), Zn$_{0.925}$Ti$_{0.075}$O (10 mol %), temperature—110 °C, catalyst amount and time specified as given, isolated yields*. 

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involving a variety of activated phenols with various β-ketoesters at 110 °C. As shown in Table 4, high yields of coumarins (3a–3x) up to 89% were obtained upon reacting β-ketoesters with various phenols. Initially, phloroglucinol, pyrogallol, 2-methyl resorcinol, orcinol, 4-chloro resorcinol, and resorcinol (1a–1f) on reaction with EAA (2a) gives corresponding coumarins in 76–89% yields (Table 4, entry 3a–3f). When m-methoxy phenol (1g) and m-cresol (1h) reacted with EAA, it requires longer reaction time (5 h) and gave the corresponding product with 69 and 65% yield, respectively (Table 4, entry 3g–3h), whereas, p-cresol (1i) gave only 58% yields under similar reaction conditions (Table 4, entry 3i). However, the polycyclic aromatic compounds such as α-naphthol (1j) reacted only with EAA and gave the corresponding coumarin in low yields (Table 4, entry 3j). It is also observed that the catalyst does not show any activity toward the nonsubstituted phenol. Afterward, ethyl butyrate (2b) smoothly reacted with various phenols (1a–1g) and gave corresponding products in good yields up to 87% (Table 4, entry 3k–3q) same as that of EAA, while ethyl benzoyl acetate (2c) gave yield of the corresponding product in 64–85% with various phenols (Table 4, entry 3r–3x). It is observed that the reaction of ethyl benzoyl acetate (2c) requires longer reaction of 5 h because of the low electrophilicity of the carbonyl carbon due to the presence of the phenyl ring adjacent to the carbonyl carbon. Similarly the naturally occurring ayapin derivatives were also synthesized using sesamol (1k) and β-ketoesters (2b–2c) under the standard reaction conditions which yields of 68 and 63%, respectively (Table 4, entry 4a–4b). The above substrate scope study reveals that, the Zn0.925Ti0.075O NPs displayed better catalytic activity in the synthesis of coumarin and ayapin by Pechmann condensation with variously activated phenols.

**Plausible Reaction Mechanism for the Synthesis of Coumarin.** The reaction pathway for the synthesis of coumarin through Pechmann condensation is represented in Scheme 1, and the mechanism for the reaction is assumed to be the same as proposed by using Zn0.925Ti0.075O NPs as a Lewis acid.40 Initially, reaction proceeds with the nucleophilic attack of the hydroxyl group of phloroglucinol on the activated EAA, resulting in the formation of the intermediate and byproduct ethanol. The formed intermediate rapidly undergoes cyclization through Lewis acid-catalyzed intramolecular condensation and followed by dehydration which yields 5,7-dihydroxy-4-methyl-2H-chromen-2-one.

**Recyclability Study.** The recycle study of Zn0.925Ti0.075O NPs in the coumarin synthesis as illustrated in Figure 2; the reaction was performed using EAA and phloroglucinol under standard optimized reaction conditions as a model substrate for Pechmann condensation. In repeated experiments, the catalyst was washed with ethanol and dried at 100 °C and used without any activation. The results of these experiments showed that the catalytic activity of Zn0.925Ti0.075O NPs did not decrease significantly even after seven catalytic cycles. Thus, the catalyst was quite stable under the reaction conditions.
However, the decrease in the activity could be due to handling losses of the catalyst after each run, as the initial catalyst charges was only 10 mol %.

**Stability of the Zn$_{0.925}$Ti$_{0.075}$O NPs.** The stability of the Zn$_{0.925}$Ti$_{0.075}$O catalyst was confirmed by studying the X-ray powder diffraction spectrum (XRD) of fresh and used catalyst samples and is presented in Figure 3; the diffraction patterns of the prepared catalyst and the fresh catalyst were found to be the same and they show the high chemical stability of the Zn$_{0.925}$Ti$_{0.075}$O catalyst.

**CONCLUSIONS**

In summary, Zn$_{1-x}$Ti$_x$O NPs was reported as an efficient, recyclable, and heterogeneous catalyst for the synthesis of coumarin using Pechmann condensation. Among the different Ti(IV)-doped ZnO catalytic systems, Zn$_{0.925}$Ti$_{0.075}$O showed rapid activation of $\beta$-ketooesters. The catalyst system was proven over a broad substrate scope with various $\beta$-ketooesters and activated phenols under the optimized reaction conditions. This synthetic methodology also extends for the synthesis of ayapin derivatives from the sesamol and various $\beta$-ketooesters. Zn$_{0.925}$Ti$_{0.075}$O NPs were stable and shows catalytic performance even after seven runs without significant loss in the % yield of the products.

**MATERIALS AND METHODS**

All required chemicals were purchased from Aldrich, Thomas Baker, and Finar and used as received without any further purification. $^1$H and $^{13}$C NMR spectra were recorded in the solvent DMSO-$d_6$ on a Bruker ADVANCE-III 500 MHz spectrometer using TMS as an internal standard.

**Synthesis of ZnO and Zn$_{1-x}$Ti$_x$O NPs.** The catalysts were prepared by the solution-free mechanochemical method. In a typical experimental procedure, zinc acetate (50 mmol) and oxalic acid (60 mmol) were mixed and ground together for 1 h at room temperature. Next, the zinc oxalate dihydrate [Zn(C$_2$O$_4$)$_2$·H$_2$O] precursor was calcined at 600 °C for 2 h in air to obtain ZnO NPs. The Zn$_{1-x}$Ti$_x$O catalysts were similarly obtained by the addition of an appropriate quantity of titanium isopropoxide in the preparation of the precursor. Zn$_{1-x}$Ti$_x$O containing 25, 50, 75, and 100 mmol Ti(IV) were synthesized.

**General Procedure for Pechmann Condensation.** In a round bottom flask, the mixture of chlorogluconic (2 mmol), EAA (2 mmol), and Zn$_{0.925}$Ti$_{0.075}$O NPs (10 mol %) was heated with constant stirring at 110 °C for the appropriate time. The progress of the reaction was monitored by the thin-layer chromatography analysis. After completion of the reaction, the mixture was dissolved in ethyl acetate, and the catalyst was separated by centrifugation. The solvent was then removed under reduced pressure, and the resulting crude product was purified by recrystallization using ethanol.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00257.

Copy of $^1$H NMR and $^{13}$C NMR of all synthesized compounds (PDF)

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**Notes**

The authors declare no competing financial interest.

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