

Synthesis of 4-(trifluoromethyl) coumarins using nano sulfated-titania as solid acid catalyst under solvent-free conditions

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ABSTRACT

Nano sulfated titania was tested as solid acid heterogeneous catalyst for the synthesis of 4-(Trifluoromethyl) coumarin and coumarin derivatives under solvent-free condition. Factorial design evidenced a positive effect of reaction temperature, amount of catalyst, and solvents. This nano-sized sulfated titania has been prepared by a sol-gel hydrothermal process. The prepared sulfated titania showed high catalytic activity in the synthesis of 4-(Trifluoromethyl) coumarin and coumarin derivatives. This method is of great value because of its environmentally benign character, easy handling, high yields, convenient operation, and green. FT-IR studies show that the catalyst can be reused for acylation without loss of catalytic activity.

Keywords: Nano sulfated-titania, Coumarins, Pechmann reaction, Solvent-free condition.

1. Introduction

Coumarin and its derivatives are widely distributed in nature and are found in all parts of plants. [1] These compounds are especially common in grasses, orchids, citrus fruits, and legumes. [2,3] They also have varied bioactivities, for example, inhibitory of platelet aggregation, [4] antiviral, [5] anticancer, [6] inhibitory of steroid 5 α -reductase [7] and inhibitory of HIV-1 protease. [8] Coumarins have been synthesized by several routes including Pechmann, [9] Perkin, [10] Knoevenagel, [11] Reformatsky, [12] Wittig reactions, [13] and by flash vacuum pyrolysis [14]. Among these, the Pechmann reaction is the most simple and widely used method, involving reactions between activated phenols and a carboxylic acid or ester containing a β -carbonyl group through an acid catalyzed transesterification, Keto-enol tautomerization, Michael addition and lastly an acid catalyzed dehydration. [15] Generally, different acid catalysts like H₂SO₄, P₂O₅, FeCl₃, ZnCl₂, POCl₃, AlCl₃, PPA, HCl, Phosphoric acid and trifluoroacetic acid are known to affect this reaction [16]. Most of these acid catalysts suffer from severe drawbacks including the use of a large amount of catalyst (for example, sulfuric acid in 10-12

equivalents, [16f] trifluoroacetic acid in three to four equivalents [16b] and phosphorus pent oxide in five-fold excess, [16g] long reaction times, temperatures to the extent of 150°C, and in some cases gave low yields.

Heterogeneous catalysts, during recent past, have also been used for the synthesis of coumarins such as Nafion, [17] PFPAT, [18] PMSCl, [19] ionic liquids, [20] mesoporous zirconium phosphate, [21] ZrOCl₂/SiO₂, [22] [N₁₁₂OH][HSO₄], [23] Zr-TMS, [24] and etc. [25] These solid acid catalysts have disadvantages like poor thermal stability and small pores for large-size reactions for which a large amount of catalyst is required to produce high yield. For example, zeolite [25a] is required in stoichiometric amount for better yield, Nafion [17] catalysts are not thermally stable, sulfated zirconia is moisture sensitive, sulfonic acid functionalized over Zr-TMS [24a] requires a high temperature for a long time with low yield, and in most previously reported methods, the Pechmann condensation reaction was limited to methyl/ethyl keto-esters. In this regard, sulfated Titania may act as an important alternative solid acid catalyst with high thermal stability, high tolerance ability, safe and easy handling, and easy preparation.

Recently, we have reported the synthesis and characterization of nano sulfated Titania (TiO₂/SO₄²⁻) having a high specific surface area with excellent

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catalytic activity towards organic reactions [26]. Now, herein, we report the study of the Pechmann condensation reaction of different substituted phenols with β -Ketoesters to produce coumarins using the nano sulfated Titania as solid catalyst in solvent-free condition. The effect of solvent, molar ratio of reactants, amount of catalyst, reaction temperature and time were investigated.

2. Experimental

2.1. Catalyst preparation

Sulfated-TiO₂ nano powder was prepared by the sol-gel process. Titanium iso-butoxide (98 % Fluka) was used as the source of TiO₂. An amount, 14.3 mL, of Ti(OC₄H₉)₄ was hydrolyzed in 150 mL water containing 1.25 mL nitric acid (65% Merck) and then the aqueous solution was stirred continuously at room temperature for 2 h to form a highly dispersed sol, and then the sol was concentrated and dried at 60°C. Sulfation was done using 0.5 M sulfuric acid solution (2.0 g mL⁻¹). The samples, after 2 h drying at 110°C, were calcined for 5 h at 500°C.

2.2. General procedure for the Pechmann condensation using sulfated-TiO₂

A mixture of the phenolic compound (1 mmol), β -keto ester (1 mmol) and nano sulfated titania (0.2 g; ~0.015 mol %) was stirred at 100°C in an oil bath for the desired time as indicated in Table 2. The reaction was monitored by TLC, and then reaction mixture was diluted with EtOAc (10 mL) and centrifuged to remove the catalyst to obtain the crude product. The crude product was purified by column chromatography on silica gel (petroleum ether: ethyl acetate; 10:1, products **3g-3n**) or recrystallized from ethanol/water (9:1) (entries **3a-f**) to afford the pure coumarin derivatives. The compounds are well known and in agreement with spectral and physical data (See supplementary data).

3. Results and Discussion

3.1. Catalyst characterization

Nano TiO₂/SO₄²⁻ was prepared by sol-gel method as we reported previously [26]. So, the textural properties

of nano TiO₂/SO₄²⁻, used in the present study are given in brief. Analysis of the SEM and TEM images of this catalyst reveals that particles are uniformly distributed in a spherical shape. Hence, SO₄²⁻ ion modification preferably retarded the aggregation. This facilitates the organic transformations. It was found from XRD and TEM that the catalyst was in nanoparticles (40-50 nm) and the anatase and rutile phases of TiO₂ confirmed and sulfated modification did not change the phases. The surface area was found to be 218 m²/g. From TGA ~0.7% decreasing in the weight of the sulfated-TiO₂ at about ~100°C is related to desorption of water molecules from the catalyst substrate. The XRD, TEM and TGA of are shown in Nano TiO₂/SO₄²⁻ Fig. 1.

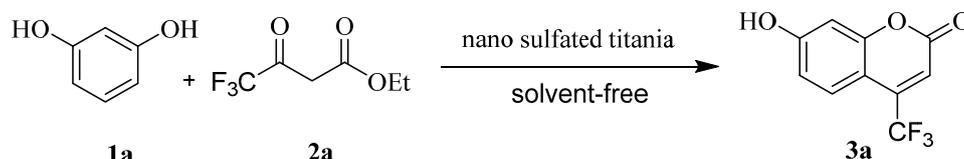
3.2. Pechmann condensation of phenolic compounds

To study the efficiency of nano sulfated titania as a catalyst for Pechmann condensation, the reaction of resorcinol (**1a**) and ethyl 4,4,4-trifluoroacetoacetate (**2a**) was selected as a model (Scheme 1).

3.2.1. Effect of catalyst amount

To optimize the amount of catalyst for the synthesis of 7-hydroxy-4-trifluoromethyl-coumarin (**3a**), the reaction between resorcinol (**1a**) and Ethyl 4,4,4-trifluoroacetoacetate (**2a**) was carried out at 100°C for 100 min under solvent-free conditions using varying amount of catalyst as shown in Fig. 1. The yield of product **3a** increased progressively from 45 % to 95 % with increasing the catalyst amount from 0.05 g (0.0037 mol %) to 0.2 g (0.015 mol %), as expected (Fig. 2, curves a-d). It is reasonable to assume that the interaction of the reactant molecules with the active sites of the nano sulfated titania catalyst is commensurate with increase in the amount of the catalyst in the reaction mixture and hence the availability of a higher number of active sites. However, the reaction did not show significant change with further increasing the catalyst amount from 0.2 to 0.6 g.

Therefore, only 0.2 g (0.015 mol %) of the catalyst is the required amount for the synthesis of coumarin **3a**. When similar reaction was carried out in the absence of the catalyst, only 5-10 % conversion was obtained even after 48 h.



Scheme 1

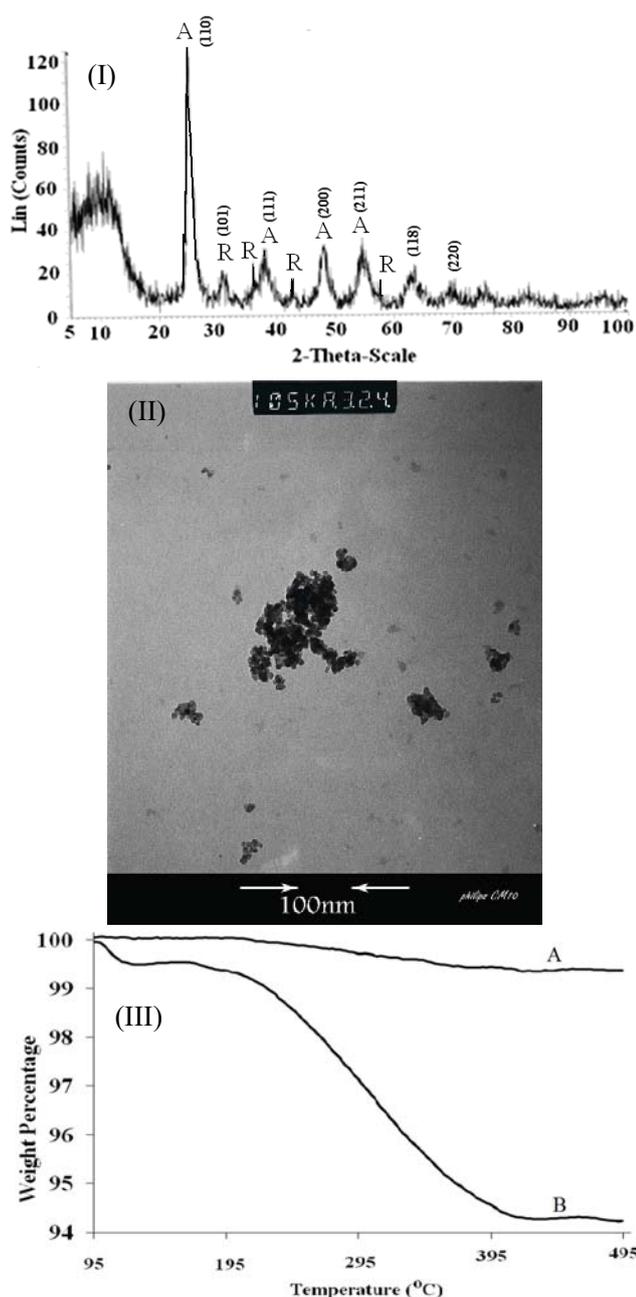


Fig. 1. (I) XRD pattern of nano sulfated-TiO₂; (II) TEM image of nano sulfated-TiO₂; (III) Thermograms revealing the thermal stability of (A) Pure TiO₂ and (B) sulfated-TiO₂.

3.2.2. Effect of temperature

The Pechmann reaction of resorcinol and methyl acetoacetate was carried out at different temperatures under solvent-free condition using 0.2 g nano sulfated titania for 100 min. Individual experiments were performed at each temperature under identical reaction conditions. In Fig. 3, the yields of product **3a** obtained at different reaction temperatures, are plotted as a

function of reactions time. As expected, the yield of product **3a** increases from 15 % to 98 % by increasing the temperature from 25°C to 160°C (Fig. 3, curves a-e). This indicates that the catalyst is quite stable and the reaction was free from the diffusion limitation at higher temperature. It is also evident that the active sites are activated more at higher temperatures. Therefore, the best optimized temperature was 100°C.

3.2.3. Effect of solvent

Fig. 4 shows the time dependent conversion of Pechmann reaction of resorcinol and methyl acetoacetate to produce the corresponding coumarin **3a**, using different solvents. Although the reaction in solvents such as toluene and ethanol continued for a period of 12 h at 100°C, there was only marginal increase after 2 h. The yield of product **3a** was found to be only 10 % and 15 % in toluene and ethanol, respectively. There was no product formation, when we used DMSO and H₂O as the solvent. Thus, solvent-free was the best choice for such a reaction.

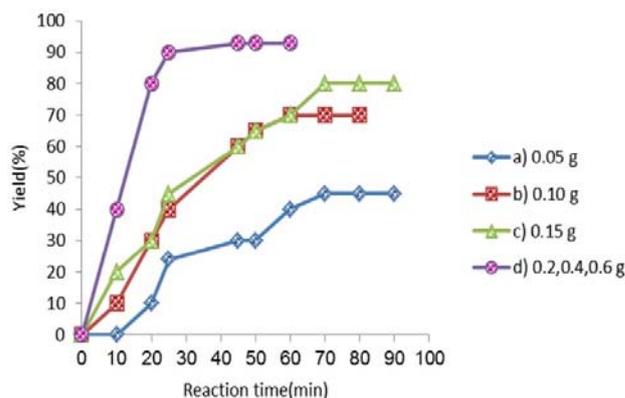


Fig. 2. Plot of yield vs reaction time for Pechmann reaction of resorcinol and ethyl 4,4,4-trifluoroacetoacetate using nano sulfated titania catalyst by different amount of catalyst.

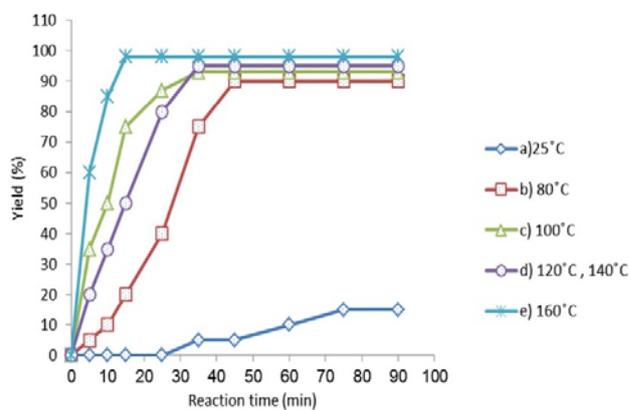


Fig. 3. Plot of yield vs reaction time for Pechmann reaction of resorcinol and ethyl 4,4,4-trifluoroacetoacetate using nano sulfated titania catalyst at different temperature.

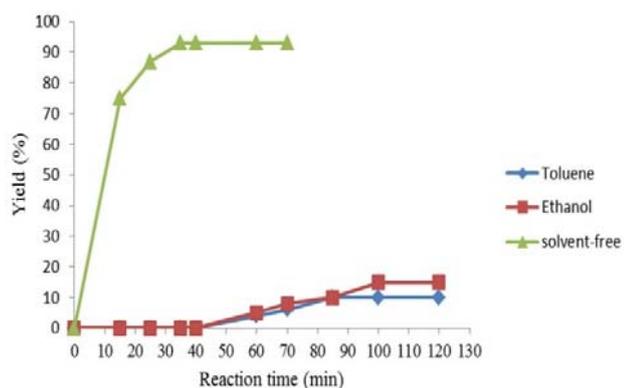


Fig. 4. Plot of yield vs reaction time for Pechmann reaction of resorcinol and ethyl 4,4,4-trifluoroacetoacetate using nano sulfated titania catalyst by using different solvents.

3.2.4. Recycle studies

To find out the reusability and stability of the catalyst, the same reaction (Scheme 1) was carried out for three times using the same catalyst under similar reaction conditions. After the reaction, the catalyst was centrifuged from the reaction mixture which was diluted by EtOAc, washed with EtOAc and reused for another three successive test runs without any further activation. The reactants were taken with respect to the amount of the catalyst recovered after each reaction cycle. The results are given in Table 1.

The yield of compound **3a** was found to decrease slowly after 3rd cycle. In order to find out the reason for the partial loss of the catalyst's activity, the catalyst samples recovered after each recycle were taken from FT-IR spectrum (Fig. 5). FT-IR spectroscopy of fresh nano sulfated titania is shown in Fig. 4a. Four bands in the region between 1230 and 980 cm^{-1} attributed to vibrational modes of bidentate sulfate ions can be seen. Two bands at 1221 and 1138 cm^{-1} appear due to asymmetric and symmetric stretching of S=O vibrations, respectively. The band around 1047 cm^{-1} is attributed to the asymmetric S-O bond. The band at 993 cm^{-1} is related to the symmetric stretching of the S-O bond. All of these bands are related to the sulfate bounds to the TiO_2 in the chelate form. The bands at 1626 and 3347 cm^{-1} are, respectively, associated with the bending and stretching vibrations of the OH group of water molecules on the surface of the solid [32]. The FT-IR spectrum of the catalyst recovered after first, second, and third reaction showed two clear bands for the bending and stretching vibrations of the -OH group of water molecules, which shows that the water molecule can be adsorbed during the work-up procedure. Also, the fifth recovered catalyst showed the bands in the range of 990-1221 cm^{-1} , which indicates the sulfonyl group.

Table 1. Recycle studied of nano sulfated titania for the preparation of **3a**.

Cycle	Time(h)	Yield (%)
Fresh	0.5	95
1 st	3	90
2 nd	4	85
3 rd	6	80

^aReaction conditions: phenol (1.0 mmol), ethyl 4,4,4-trifluoroacetoacetate (1.0 mmol), nano sulfated titania (0.015 mol%), in an oil bath at 100°C.

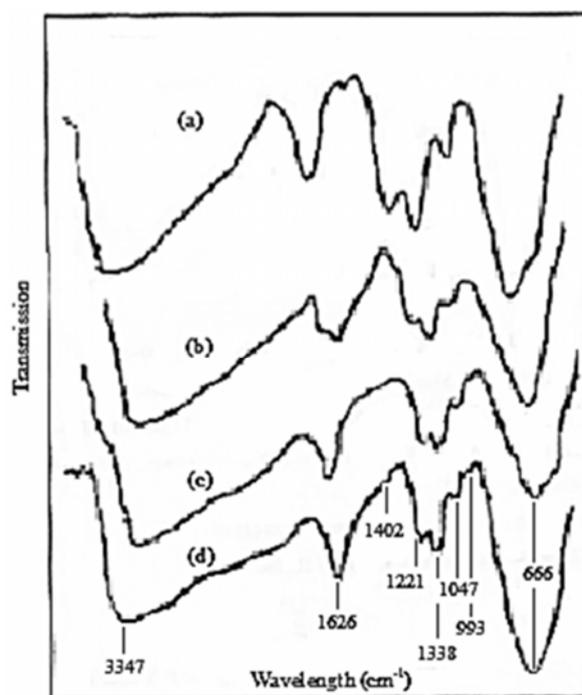
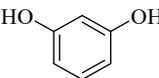
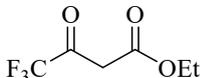
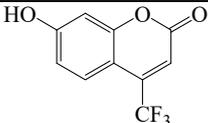
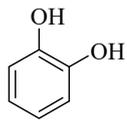
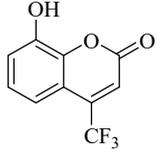
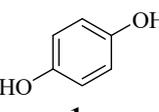
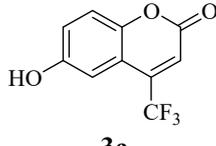
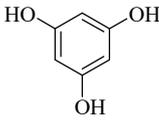
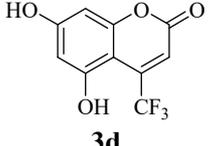
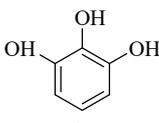
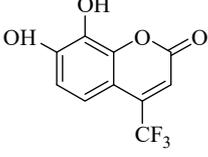
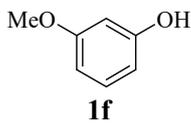
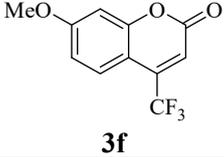


Fig. 5. FT-IR spectra of the (a) fresh, (b) first, (c) second, and (d) third recycle of nano sulfated titania.

3.2.5. Effect of different substrate

Due to its better catalytic activity for the Pechmann condensation of resorcinol and ethyl 4,4,4-trifluoroacetoacetate to 7-hydroxy-4-trifluoromethyl-coumarin, nano $\text{TiO}_2/\text{SO}_4^{2-}$ was used as the catalyst for the condensation of a series of phenol with β -ketoesters under optimized reaction conditions (Table 2). As shown in Table 2, nano sulfated titania proved to be active towards all substrates. Then, in order to show the generality and originality of the present catalyst for the synthesis of coumarins, different β -ketoesters such as methyl acetoacetate, ethyl acetoacetate, vinyl acetoacetate, and etc. were examined. (Table 3).

Table 2. Synthesis of 4-(Trifluoromethyl)-coumarin using nano sulfated-TiO₂ under solvent-free condition^a.

Entry	Phenol	β -Ketoester	Coumarin	Time (h)	Yield (%) ^b
1	 1a	 2a	 3a	0.5	95
2	 1b	2a	 3b	3	95
3	 1c	2a	 3c	6	95
4	 1d	2a	 3d	2	95
5	 1e	2a	 3e	2	95
6	 1f	2a	 3f	2	95

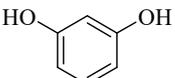
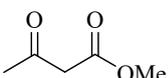
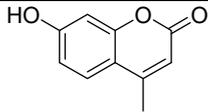
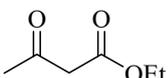
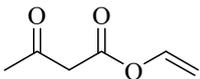
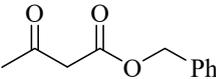
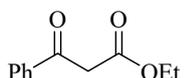
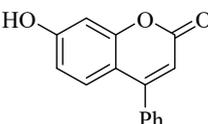
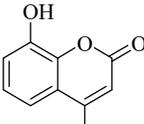
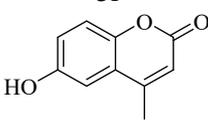
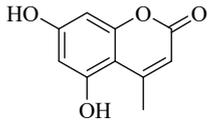
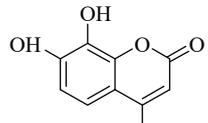
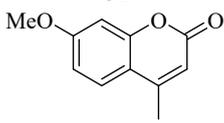
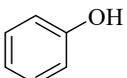
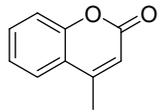
^aReaction conditions: phenol (1.0 mmol), ethyl 4,4,4-trifluoroacetoacetate (1.0 mmol), nano sulfated titania (0.015 mol%), in an oil bath at 100°C under solvent-free conditions.

^bIsolated yield.

By comparing Table 2 and 3, higher conversions were obtained when trifluoro methyl acetoacetate was used instead of other β -ketoesters. This is because of the presence of more electron-withdrawing group (-CF₃) resulting from more electropositive β -keto carbonyl group. Hence, the attack of nucleophile will be more facile. From Table 3, it is evident that the presence of activated group and position of the activated group in phenol ring has great influence on the yield of coumarins. Catechol (**1b**) and *p*-hydroxy phenol (**1c**) were less active than that of resorcinol (**1a**), nevertheless all substrates have one electron donating hydroxyl group. This may be due to the presence of hydroxyl group of resorcinol at meta-positions activates the aromatic ring more than that of at *ortho*,

and *para*-positions. Activity decreased gradually with decreasing of strength of ring activating group. Phenol was less reactive than other substituted phenols studied here. Reports on Pechmann condensation involving phenol are rare. Tyagi *et al.* [33] reported that the reactivity of phenol over sulfated zirconia was not good even using microwave irradiation, whereas mesoporous zirconium phosphon-ate resulted in 4-methyl-coumarin with only 57 % yield [21]. In addition, 3-Methoxy phenol showed no detectable demethylation under the given conditions. However, some of other previous methods reported in the literature showed significant demethylation at high temperature [34]. Phenol requires a longer reaction time, as no electron-donating group is present.

Table 3. Synthesis of coumarin derivatives using nano sulfated-TiO₂ under solvent-free condition.

Entry	Phenol	β -Ketoester	Coumarin	Time (h)	Yield (%) ^b
1	 1a	 2b	 3g	0.5	93
2	1a	 2c	3g	0.5	90
3	1a	 2d	3g	1	90
4	1a	 2e	3g	0.75	90
5	1a	 2f	 3h	5	0
6	1b	2b	 3i	6	90
7	1c	2b	 3j	8	90
8	1d	2b	 3k	3	95
9	1e	2b	 3l	3	95
10	1f	2b	 3m	2	80
11	 1g	2b	 3n	24	70

^aReaction conditions: Phenol (1.0 mmol), β -ketoester (1.0 mmol), nano sulfated titania (0.015 mol%), 100°C, solvent-free conditions.^bIsolated yield.

3.2.6. Comparison of activity of nano sulfated-titania with various catalysts for the synthesis of coumarin derivatives.

For the purpose of comparison, the performances of nano sulfated-titania and some other catalysts in the synthesis of 7-hydroxy-4-methyl-coumarin is also shown in Table 4. It can be seen that nano sulfated-titania demonstrates the superior performance towards synthesis of coumarin derivatives, and the promising features in terms of easy separation of the catalyst, reaction rate, product yield, low catalyst loading, and reaction temperature in comparison with the existing systems.

4. Conclusion

In conclusion, we have developed a simple and efficient method for the synthesis of substituted coumarins via Pechmann condensations using nano sulfated-TiO₂ catalyst under solvent-free conditions. Moreover, the low cost of the catalyst, solvent-free condition, low toxicity of the catalyst, simple experimental procedure, and recyclability of the catalyst and high yields of the products are the advantages. We believe our procedure will find important applications in the synthesis of coumarins and the method is environmentally benign.

Acknowledgements

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Table 4. Comparison of activity of nano sulfated-titania with some other catalysts in the synthesis of 7-hydroxy-4-methyl-coumarin under solvent-free condition.

Entry	Catalyst	Temp. (°C)	Time (min)	Isolated yield (%)	Ref.
1	Nano sulfated-titania	100	30	95	This work
2	[N ₁₁₂ OH][HSO ₄]	90	180	99	[23]
3	m-ZrP	160	240	94	[21]
4	Fe ₃ O ₄ @SiO ₂ @PrSO ₃ H	130	130	25	[35]
5	HClO ₄ SiO ₂	130	35	95	[36]
6	SBPDSA	80	10	90	[37]
7	SBSSA	80	15	87	[38]

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