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Efficient One-pot Synthesis of 4 Hydroxy-2H Chromene by heterogeneously catalyzed ZnO NP and mesoporous aluminosilicate catalysts in solvent free condition.

Birendra Nath Mahato^a, T. Krithiga.^{a*}, J. Aravind Kumar^b, G. Yogalakshmi^a

Mr. Birendra Nath Mahato

PhD Scholar

Department of chemistry, Sathyabama Institute of Science and Technology, Chennai-600119, India.

e-mail: birendran1@gmail.com, Contact No. +917978068818

Dr. T. Krithiga

Associate Professor

Department of chemistry, Sathyabama Institute of Science and Technology, Chennai-600119, India

e-mail: krithi_t2001@yahoo.com, krithiga.chemistry@sathyabama.ac.in

Ms. G. Yogalakshmi

M.Sc Student

Department of chemistry, Sathyabama Institute of Science and Technology, Chennai-600119, India

e-mail: krithi_t2001@yahoo.com, krithiga.chemistry@sathyabama.ac.in

Dr. Aravind Kumar

Assistant Professor

Department of Chemical Engineering, Sathyabama Institute of Science and Technology, Chennai-600119, India

e-mail: aravindjsbu@gmail.com

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^a*Department of Chemistry, Sathyabama Institute of Science and Technology, Chennai-600119, India.*

^b*Department of Chemical Engineering, Sathyabama Institute of Science and Technology, Chennai-600119, India.*

*Corresponding Author

Dr. T. Krithiga

Fax: 044-24502344

Tel: 044-24503150, Mobile: +919176672094.

Email: krithi_t2001@yahoo.com, krithiga.chemistry@sathyabama.ac.in

Abstract

4-Hydroxy-2H Chromenes are fused benzopyran rings, an important class of biologically active compounds, widely used as antibacterial, antiviral, antitumor, and anticancer agents. In this present paper, we report the 4-Hydroxy-2H Chromenes synthesis by using two catalysts namely, (i) ZnO nanoparticles and (ii) mesoporous ZnO/AlSBA-15 (7) catalysts. The ZnO NP catalyst was prepared by using leaf extract while ZnO/AlSBA-15(7) catalysts were prepared by the wet chemical route. All catalysts were characterized by XRD, SEM, EDS, FTIR, and N₂ sorption techniques. The catalytic activity of the synthesized catalyst was evaluated in the one-pot reaction using aromatic aldehyde and Coumarin, and found to be maximum yield of 81% at temperature 80°C, a catalyst dose of 10 mmol %, in time limit of 4h.

Keywords: One-pot Synthesis; Mesoporous ZnO/ AlSBA-15(7) catalyst; Green synthesis of ZnO; 4 Hydroxy-2H Chromene scaffolds.

1. Introduction

One-pot synthesis are promising techniques in organic synthetic chemistry owing to numerous advantages such as process simplicity, convenient work-up, economical, minimum solvent, and desired products in a single pot with the required quantity [1-4]. Moreover, the use of water instead of solvent in the organic reaction is an important and growing field of research in recent times. 4-Hydroxy-2H-Chromene (fused benzopyran) are an important class of heterocyclic compound which have shown biological activities, antihypertensive, cardio protector, and insecticides [5-11, 20, 21]. Additionally, 4-Hydroxy-2H Chromene derivatives are also used in cosmetics, pigments, and agrochemicals [12, 13]. Owing to the enormous application of the 4-Hydroxy-2H Chromene derivatives, there is a need for an efficient catalyst that could make the transformation reaction easier, selective, and high yield-oriented. Till date, available procedure of chromene derivatives includes Pechmann, Reformatsky, Perkin, Knoevenagel, and Wittig reaction. Among these, the Knoevenagel condensation route is most preferred method [42], in which generally acid catalyst such as OBS, SDS, TBAB, Sulphonated catalyst, fluoride, chloride etc was employed [36-43].

Heterogeneous catalysis plays a crucial role in organic synthesis because of many advantages over homogeneous catalysis counterparts, such as recyclability,

regeneration, process simplicity ^[14]. Besides, it is an important protocol of the green chemistry principle. In this regard, the researcher always endeavors for designing and fabricating a superior and effective heterogeneous catalyst. Certainly, it is a great challenging task for the researcher. For this purpose researchers often use a suitable metal dispersed in a supporting material to enhance the effectiveness, selectivity, and yield of the product. Moreover, SBA-15 is an outstanding and excellent 2D mesoporous material widely used in adsorption, catalysis, and preparation of fine chemicals owing to high surface area (1000 m²/g), tunable pore size (3-30nm), thick wall, greater hydrothermal stability (up to 800 deg. C), and greater accessibility ^[15-19]. The acidity of SBA-15 can be enhanced by incorporating various functional groups or metal atoms during the synthesis or by the post-grafting method. For example, Muthukumaran et al show that AISBA-15 is more acidic than SBA-15 while retaining the structural properties ^[17]. Therefore, functionalized SBA-15 catalyst has been extensively used in variety of catalysis process.

Recently, the Green synthesis of noble metal and metal oxide nanoparticles using plant extract has much attention in the research field owing to environment-friendly, energy-saving, utilization of abundant natural resources, and green protocol. It is believed that the plant part contains organic compounds such as polyphenol, saponin, tannin, and so on which act as reducing agents and capping agents in the synthesis of nanoparticles ^[25]. The low-cost metal oxide such as ZnO, CuO, TiO₂, CeO₂, and Fe₂O₃ nanoparticles are extensively exploited due to their unique physic-chemical properties, for example, Abdullah et al synthesized the Fe₂O₃ nanoparticle using phoenix dactylifera leaf extract having a spherical shape with an average crystallite size of 12.61nm^[30]. For instance, ZnO nanoparticles are a versatile compound that possesses a broad spectrum of properties and is extensively applied in adsorption^[29], catalysis ^[23,28], photocatalysis ^[25], semiconductor materials, electronic devices, electrocatalysis, batteries, supercapacitor ^[31-33], and biomedical application ^[26,27,30,34-35]. So far, ZnO nanoparticles have been prepared by using various leaf extracts and evaluated for photocatalytic activity, biomedical application, etc. However, there is a very little number of reported works on biosynthesized ZnO for organic transformation reaction ^[23, 28]. Therefore, it is necessary to explore the catalytic activity of ZnO nanoparticles prepared from the leaf extract in organic synthesis.

With the above view, the objective of this work was to synthesize the ZnO nanoparticles using henna leaf extract, characterization of the as-synthesized nanoparticle by using the various instrumental and spectroscopic methods, and catalytic activity evaluation of ZnO nanoparticle in 4 Hydroxy-2H Chromene synthesis via the one-pot multi-component procedure. Moreover, for comparison purposes, we use our previously reported ZnO/AlSBA-15 (7) nanocomposite catalysts in activity evaluation.

2. Material and Methodology

2.1 Materials

Zinc acetate dihydrates 99.5% ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), sodium hydroxide 99% (NaOH), 4Hydroxy Coumarin 99%, Vanillin 99% ($\text{C}_8\text{H}_8\text{O}_3$), Ethyl Acetoacetate 98% ($\text{C}_6\text{H}_{10}\text{O}_3$) were purchased from Merck India Limited. All chemicals used for this study are analytical grade and without any modification.

2.2 Henna leaf extract and ZnO catalyst fabrication

A handful of *Lawsonia inermis* (Henna) leaves are collected from the local garden, washed thoroughly with Distilled water, and sun-dried for 3 days. The dried leaves were pulverized to obtain a fine powder (sieve 100 mesh) by an electric grinder. The grounded 5 g *Lawsonia inermis* powder was taken in a beaker containing 100 ml distilled water and kept in the hot plate at 80°C for 3 h under magnetically stirred conditions. Next, it was filtered off and the supernatant solution (extract) was used for the synthesis of ZnO nanoparticles [24].

Separately, 30ml of leaf extract was mixed with 100 ml of 2M zinc acetate dihydrate solutions and heated at 80°C for 30 minutes. The pH of the solution was adjusted to 11 by using a 2M NaOH solution while stirring. Next, the mixture was left for another 30 min under stirring conditions maintaining the temperature. The white crystalline precipitate of zinc oxide was formed, which was then separated by filtration. The precipitate was washed using water and dried in a hot air oven at 100°C. The ZnO nanoparticles obtained were used as a green catalyst.

2.3 ZnO/AlSBA-15 (7) catalysts

The catalyst ZnO/AlSBA-15 (7) was prepared by hydrothermal method and characterized XRD, SEM, BET surface area, FTIR, TPR- H_2 in our previous studies [18]. We used the material in this study for comparison purposes in catalytic studies.

2.4 Characterization techniques

The XRD spectrum was recorded by using an Advance D8 (Bruker) X-ray diffractometer in the 2θ range from 10° - 90° , using Cu $k\alpha$ source ($\lambda=1.54\text{\AA}$) at the scan step rate of 0.02. The SEM image was recorded by FEI QUANTA 200 FEG High-Resolution SEM (HR-SEM). FT-IR spectrum of the catalyst was performed on the Bruker Alpha - T in the range $400\text{--}4000\text{ cm}^{-1}$. The N_2 Adsorption-desorption data were recorded in Nova e 2200, (Quantachrome) attached with ASiQwin software. Before analysis, the sample was degassed at 100°C for 2h. The surface area was estimated by using the Brunauer-Emmett-Teller (BET) equation. The 2H Chromene adduct was characterized by FT-IR (Bruker Alpha-T) in the wavelength range $400\text{--}4000\text{ cm}^{-1}$ and the proton NMR spectrum was recorded in Bruker 400 MHz NMR instrument.

2.5 Determination of catalytic activity in the one-pot synthesis reaction.

The catalytic activity of prepared ZnO NP and ZnO/AlSBA-15 (7) catalysts was evaluated in the one-pot synthesis of 4-Hydroxy-2H Chromene derivative. The chromene was prepared by using method as described elsewhere [42]. Typically, a mixture of vanillin (1mol), 4-hydroxy coumarin (2mol), and catalysts were added in a three-neck round bottle flask and refluxed at 80°C for 60 min. Using water (10ml) as a solvent (Scheme-1). The reaction was monitored by TLC and on completion, the solvent was evaporated and crystallized with ethanol to get pure product [35].

Scheme-1. 4-Hydroxy 2H- Chromene synthesis

3. Result and Discussion

3.1 Catalyst characterization by XRD

The XRD pattern of ZnO NP is illustrated in Fig-1(a). The peaks at 2θ values of 31.84° , 34.50° , 36.40° , 47.60° , 56.67° , 62.94° , 66.44° , 68.06° , 69.19° , 72.65° , and

76.99° correspond to the hexagonal wurtzite phase of (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) of zinc oxide nanoparticles. However, the obtained peaks are minutely right side distorted of JCPDFWIN file –PDF #653411, which may be due to high pH maintained during the synthesis. The low angle XRD pattern of ZnO/AlSBA-15 (7) is illustrated in Fig-1 (b). The three characteristic peaks (100) (110) and (200) indicate long-range mesoporous with 2D hexagonal symmetry (Space group $P6mm$).

Fig-1(a). XRD Pattern of ZnO nanoparticle.

Fig-1(b) Low angle XRD pattern of ZnO/AlSBA-15(7)

3.2 Catalyst characterization by SEM

The SEM image of Zinc oxide nanoparticles is illustrated in Fig.-2. The image depicts that the ZnO nanoparticle obtained has a spherical shape. The SEM image shows the presence of agglomerates of ZnO nanoparticles. This is due to the high surface energy of nanoparticles. The EDAX image of ZnO nanoparticle is shown in Fig-3. The EDAX spectrum confirms the presence of Zn and O in the catalyst.

Figure-2 SEM image of ZnO nanoparticle.

Fig-3 SEM EDX of ZnO nanoparticle

3.3 Catalyst characterization by FTIR

The FT-IR spectrum of ZnO nanoparticles is illustrated in Fig.4. The IR vibrational frequencies obtained at 3387 cm^{-1} , 1636 cm^{-1} , 1499 cm^{-1} , 1400 cm^{-1} ,

and 539 cm^{-1} correspond to O-H stretching of an adsorbed water molecule on zinc oxide, C=O stretching, water and CO_2 molecule adsorption on ZnO surface, O-H in-plane bending of carboxyl group adsorbed on ZnO and metal-oxygen bond Zn-O stretching respectively. The peak at 539 cm^{-1} is the characteristic peak for ZnO nanoparticle

Fig-4. FTIR spectrum of ZnO nanoparticles.

3.4 BET studies

The surface properties of ZnO NP catalyst were evaluated by N_2 Adsorption-desorption isotherm studies and the obtained graph is depicted in Fig-5. The catalyst shows type IV isotherm. The isotherm shows that at low pressures the micropore is filled with gas and with the increase of pressure it starts to form multilayers. At high pressure, the capillary condensation prevails. The calculated surface area was found to be $31\text{ m}^2/\text{g}$. The isotherm indicates the ZnO NP catalyst shows a hysteresis loop of type H3.

Fig-5. N₂ Sorption Isotherm of ZnO nanoparticles.

3.5 Catalytic activity test

3.5.1 Effect of catalyst dose on 4Hydroxy-2H Chromene synthesis

Effect of catalyst amount was investigated in 4Hydroxy-2H Chromene synthesis by varying the catalyst amount while keeping other parameters constant. The obtained data was illustrated in table-1. It is evident that in the case of catalyst-free reaction the yield was negligible. In the presence of a catalyst, the 2H-Chromene conversion reaction occurs and 10 mol % catalysts are found to be an optimum catalyst dose for both the catalysts ZnO NP and ZnO/AlSBA-15(7).

Table-1, Effect of catalyst on the 4Hydroxy-2H Chromene synthesis

Sl.No.	Aromatic aldehyde	Catalyst type	Catalyst (mol %)	Time (h)	Yield ^a (%)
1	Vanillin	ZnO NP	Free	2	Trace
2	Vanillin	-do-	5	2	48
3	Vanillin	-do-	10	2	78
4	Vanillin	-do-	15	2	79
5	Vanillin	ZnO/AlSBA-15(7)	Free	2	Trace
6	Vanillin	ZnO/AlSBA-15(7)	5	2	56
7	Vanillin	ZnO/AlSBA-15(7)	10	2	81
8	Vanillin	ZnO/AlSBA-15(7)	15	2	81

^aIsolated yield calculated after recrystallization, Reaction condition: vanillin (1mol), 4-hydroxy coumarin (2mol) catalyst: ZnO NP and ZnO/AlSBA-15, Solvent: water (10ml)

Fig-6. Synthesis of 4-Hydroxy 2H- Chromene-2-one

3.5.2 Effect of time on 4Hydroxy-2H Chromene synthesis.

For the study of the effect of time on reaction, the reactions were conducted for 1h, 2h, 3h, and 4h by using ZnO NP and ZnO/AlSBA-15(7) catalysts separately. Table-2 illustrates the effect of different periods on reaction yields. It is evident that, in the case of ZnO NP, the 4h reaction time gives a maximum yield of 80 %, whereas the ZnO/AlSBA-15(7) catalyst yields 81% in 3h time.

Table-2 Effect of Time on 4Hydroxy-2H Chromene synthesis.

Sl.No.	Aromatic aldehyde	Catalyst type	Solvent (10 ml)	Time (h)	Yield ^a (%)
1	Vanillin	ZnO NP	Water	1	65
2	Vanillin	ZnO NP	Water	2	79
3	Vanillin	ZnO NP	Water	3	79
4	Vanillin	ZnO NP	Water	4	80
5	Vanillin	ZnO/AlSBA-15(7)	Water	1	72
6	Vanillin	ZnO/AlSBA-15(7)	Water	2	81
7	Vanillin	ZnO/AlSBA-15(7)	Water	3	81
8	Vanillin	ZnO/AlSBA-15(7)	Water	4	81

^aIsolated yield calculated after recrystallization, Reaction condition: vanillin (1mol), 4-hydroxy coumarin (2mol) catalyst (10 mol%): ZnO NP and ZnO/AlSBA-15, Solvent: water (10ml)

3.5.3 Effect of Temperature on 4Hydroxy 2H- Chromene synthesis.

To investigate the effect of temperature on 2H Chromene synthesis, the reaction was conducted at an increment of 10°C starting from 50°C. From table-3, it was evident that with the rise of reaction temperature from 50 to 60 °C, the yield was increased to 77% from 58% for ZnO NP catalyst. The optimum yield was found at 80°C for the ZnO NP catalyst. Similarly, in the case of the ZnO/AlSBA-15(7) catalyst, the yield was increased from 60 to 74 % while increasing the reaction temperature from 50 to 60°C. The maximum yield of 81 % was obtained at 70°C. Further increase in temperature does not enhance the yield. Therefore, it can be concluding that both the catalyst showing good yield at low temperature. However, ZnO/AlSBA-15(7) showing a little more superior effect in the context of lower working temperature.

Table-3 Effect of Temperature on 4Hydroxy-2H Chromene synthesis

Sl.No.	Aromatic aldehyde	Catalyst type	Solvent (10 ml)	Temp.(°C)	Yield ^a (%)
1	Vanillin	ZnO NP	Water	50	58
2	Vanillin	ZnO NP	Water	60	77
3	Vanillin	ZnO NP	Water	70	79
4	Vanillin	ZnO NP	Water	80	81
5	Vanillin	ZnO/AlSBA-15(7)	Water	50	60
6	Vanillin	ZnO/AlSBA-15(7)	Water	60	74
7	Vanillin	ZnO/AlSBA-15(7)	Water	70	81
8	Vanillin	ZnO/AlSBA-15(7)	Water	80	81

^aIsolated yield calculated after recrystallization, Reaction condition: vanillin (1mol), 4-hydroxy coumarin (2mol) catalyst (10 mol%): ZnO NP and ZnO/AlSBA-15, Solvent: water (10ml)

To show the efficiency of present method, we have compared our results obtained from the synthesis of 4-Hydroxy 2-H-chromene catalyzed by ZnO NP and

ZnO/AlSBA-15 with some of the other results reported in literature. As it can be seen in table-4, some of the documented procedure have used hazardous reagents (table-4, entry-8) and solvents ethanol. Furthermore, it has been found that in the absence of catalyst, the reaction is incomplete and sometimes takes longer time to formed the product with little efficiency.

Table-4 Comparison of various previously documented catalyst for 4-Hydroxy 2-H-chromene derivative synthesis.

Entry	Catalyst	Reaction condition	Time,min.	Yield	Reference
1	<i>Fe₃O₄@SiO₂@ImbisethylFc[HC₂O₄]</i>	<i>EtOH:H₂O; Reflux</i>	<i>60</i>	<i>88-96</i>	<i>36</i>
2	<i>Fe(SD)₂</i>	<i>20 mol% ; water ;100°C</i>	<i>7</i>	<i>79</i>	<i>37</i>
3	<i>Tetrabutylammonium bromide (TBAB)</i>	<i>10 mol%; water;Reflux</i>	<i>25-40</i>	<i>82-92</i>	<i>38</i>
4	<i>[bmim]BF₄</i>	<i>400 mol%; 60-70°C</i>	<i>120-180</i>	<i>84</i>	<i>39</i>
5	<i>SDS</i>	<i>20 mol%; water; 60°C</i>	<i>150</i>	<i>84-90</i>	<i>40</i>
6	<i>OBS</i>	<i>50 mol%;water; Reflux</i>	<i>20-50</i>	<i>74-88</i>	<i>41</i>
7	<i>DBSA</i>	<i>25 mol%; EtOH:water; 80°C</i>	<i>40-50</i>	<i>60-90</i>	<i>42</i>
8	<i>NaHSO₄.SiO₂</i>	<i>150mg; Toluene; 100°C</i>	<i>30</i>	<i>85-91</i>	<i>43</i>
9	<i>ZnO NP</i>	<i>10 mol%, water,</i>	<i>60</i>	<i>79</i>	<i>This study</i>

10	ZnO/AlSBA-15	10 mol%, 60	81	This study
water				

3.6 Spectral data of FTIR

The FTIR spectrum of 3-3' ((3-hydroxy-4hydroxyphenyl) methylene) bis(4-hydroxy-2Hchromene-2-one) is illustrated in fig-7. The peak obtained at 3494 cm^{-1} is due to OH stretching. The peak at 3073 cm^{-1} represents C-H stretching vibration frequency. The carbon hydrogen double bond vibration can be seen at 2727 cm^{-1} . The observed peak at 1346 cm^{-1} is due to -OH bending. The functional group (C=O) can be seen at 1267 cm^{-1} 763 cm^{-1} (stretching). The diminished peak at 560 cm^{-1} is due to Zn-O bond stretching.

Fig.7- FTIR Spectrum of 4 Hydroxy 2H-Chromene

3.7 Characterization of adduct by ^1H NMR.

The proton NMR spectrum of 3-3' ((3-hydroxy-4hydroxyphenyl) methylene) bis(4-hydroxy-2Hchromene-2-one) is illustrated in fig-8. The chemical shift at 2.5 δ is of aromatic Ester, at 2.7 δ is represents presence of OCH_3 group. Similarly, shift at 3.5 δ indicates the proton of -OH functional, shift at 5.5 δ represents vinylic proton and shift at 7.0-8.5 δ is due to aromatic proton.

Fig.8- ^1H NMR Spectrum of 4 Hydroxy 2H-Chromene

3.8 Recyclability of Catalyst.

The probable re-use and activity constancy of catalyst is a significant aspect of a heterogeneous catalyst. With this view, the experiment was repeated 4 times consecutively by using a used catalyst and illustrated in Fig-9. Both the catalyst can be effectively used up to the 4th run with minor loss in yield. It is obvious owing to the blockage of the pore of the catalyst. The ZnO/AlSBA-15 catalyst shows much stability in the recycling test compared to ZnO NP. There was no loss in yield in the 2nd run by ZnO/AlSBA-15 catalyst, thereafter minor loss (2%) in yield in each 3rd and 4th run. In the case of ZnO NP catalyst, there was a 2% loss in the 2nd run and stable in the 3rd run and thereafter drastically losses activity in 4th run. The yield loss was 13 % in the 4th run. Therefore, it can be concluded that the ZnO/AlSBA-15 catalyst is much stable in the recycling test compared to the ZnO NP catalyst.

Fig-9. Recyclability of ZnO NP and ZnO/AlSBA-15 (7) Catalysts.

3.9 Plausible mechanism

The mechanism of formation of 4 Hydroxy 2H-Chromene derivatives via two-component coupling strategy is generally hypothesized, to begin with, a Knoevenagel condensation between the active methylene compound and aldehyde followed by Michael addition. The reaction proceeds with initial condensation of 4 Hydroxy Coumarin in the presence of Zn species of catalyst resulting in the formation of intermediate with the loss of water molecules. The addition of another molecule of aldehyde leading to cyclization and final catalyst is removed. Fig-10 represents the plausible mechanism of the formation process.

Fig-10: Plausible mechanism of formation of 4 Hydroxy 2H-Chromene.

4 Conclusion

In conclusion, a simple, eco-friendly one-pot synthesis of 4 hydroxy 2H-Chromene syntheses were devised by using water as solvents and heterogeneous catalysts ZnO NP and ZnO/AlSBA-15(7). The catalyst was characterized by various instrumental techniques and catalytic activity was tested in the synthesis of 4 hydroxy 2H-Chromene. The reaction condition was optimized and found to be a yield of 80-81 % in 4h time, 81 % in 80°C, and yield of 78-81 % with 10 mole % catalysts. The recyclability test shows the catalysts can be used three times efficiently without giving much deviation in yields. It is imperative to mention that the reaction was conducted in a double greener way by obeying the green synthesis protocol. Finally, the mechanistic path of the reaction was proposed.

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