

CuO-CeO₂ nanocomposite as a green and efficient recyclable catalyst for the multicomponent synthesis of 2-amino-4*H*-chromene derivatives

Jalal Albadi^{a*}, Azam Mansournezhad^b and Zeinab Azarian^b

^a Behbahan Khatam Alanbia University of Technology, Behbahan, Iran

^b Department of Chemistry, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran

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Abstract: CuO-CeO₂ nanocomposite as a green and highly efficient recyclable catalyst, catalyzed multicomponent synthesis of 2-amino-4*H*-chromene derivatives under solvent-free conditions. This catalyst can be easily recovered by simple filtration and recycled up to 7 consecutive runs with consistent activity. The procedure provides some advantages such as simple work-up, clean procedure, short reaction times and high yields of the products.

Keywords: CuO-CeO₂ nanocomposite, 2-Amino-4*H*-chromene, β -naphthol, Malononitrile.

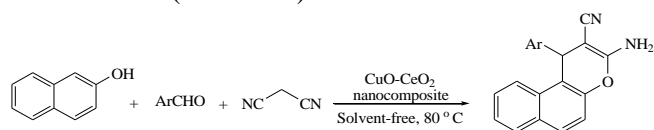
Introduction

The synthesis of 2-amino-4*H*-chromenes and their derivatives is of much importance to pharmaceutical and organic chemists. These compounds are of interest heterocyclic compounds as they have a wide range of biological properties such as spasmolytic, diuretic, anticoagulant, anticancer and antisterility agents [1-2]. Moreover, these compounds can also be employed as cosmetics and pigments [3]. 2-Amino-4*H*-chromenes are generally prepared by condensation of aldehydes, malononitrile and an activated phenol in the presence of piperidine in ethanol or acetonitrile as a reaction solvent [4]. Nevertheless, piperidine is a toxic compound and can be absorbed through the skin mucous membranes. Therefore, in order to improve the efficiency of this reaction several benign catalyst and modified procedures have also been reported [5-22]. However, some of these procedures suffer from one or more drawbacks such as use of expensive reagents, low yields of the products, use of toxic solvents, longer reaction times, tedious workup and harsh reaction conditions. Therefore, there is a scope to develop an alternative method for the synthesis of 2-amino-4*H*-

chromenes. Recently, the practical applications of nanocomposite metal oxides as catalysts in organic synthesis have increased due to their high catalytic activity resulting from their high surface area [23-24]. Nanocomposite oxides are alternative solid heterogeneous catalysts that are easily synthesized and eco-friendly. These catalysts have proved to be useful to chemists in the laboratory and in industry due to the good activation of adsorbed compounds and reaction rate enhancement, selectivity, easier work-up, recyclability of the supports and the eco-friendly, reaction conditions employed [25-28]. Because of these properties, nanocomposite oxides are extensively used as solid catalysts in various organic reactions. Recently we have reported the preparation of CuO-CeO₂ nanocomposite and its catalytic activity for the synthesis of aryl-14*H*-dibenzo[a-j]xanthenes [29]. This catalyst is safe, easy to handle and environmentally benign. In continuation of these studies and also our studies on the synthesis of benzochromene derivatives [30], herein, we wish to report the applicability of CuO-CeO₂ nanocomposite as a green, efficient and recyclable catalyst for the synthesis of 2-amino-4*H*-chromenes derivatives *via* the one-pot three-component

*Corresponding author. Tel: (+98) 6712229969, Fax: (+98) 6712229969, E-mail: Chemalbadi@gmail.com

condensation of β -naphthol with aromatic aldehydes and malononitrile (Scheme 1).



Scheme 1: Synthesis of 2-amino-4H-chromenes catalyzed by CuO-CeO₂ nanocomposite.

Results and discussion

The catalyst was synthesized by co-precipitation method and characterized by XRD, BET specific surface area, ESEM and EDS analysis [29]. For the optimization of the reaction conditions, the reaction of benzaldehyde, β -naphthol and malononitrile was chosen as the model and its behavior was studied under the various conditions. Optimization showed that the best result was achieved when the reaction of benzaldehyde (1mmol), β -naphthol (1mmol) and malononitrile (1mmol) was performed in the presence of 0.05 g of CuO-CeO₂ nanocomposite (10 mol % CuO, 90 mol % CeO₂), at 80 °C under solvent-free conditions (Table 1, entry 1). After optimization of the reaction conditions, in order to evaluate the generality

of this method, the reaction of various aromatic aldehydes, containing electron-donating and electron-withdrawing groups, was explored. In all cases, aromatic aldehydes reacted successfully and desired products achieved in good to high yields. It can be found that the kind of groups on aromatic ring have no significant effect on the reaction rate. Work-up procedure is so simple and all products were cleanly isolated with simple filtration and evaporation of solvent. Products were easily recrystallized from hot ethanol and were obtained in good to high yields during the short reaction times. Another advantage of this method is that CuO-CeO₂ nanocomposite easy to handle and its preparation is simple and straightforward. Furthermore, CuO-CeO₂ nanocomposite makes the 2-amino-4H-chromenes synthesis eco-friendly, with the possibility of scale-up to an environmentally benign and clean technology. Additionally, recyclability of the CuO-CeO₂ nanocomposite was also studied under the optimized conditions. For this purpose the reaction of benzaldehyde, β -naphthol and malononitrile was selected again as a model.

Table 1. Synthesis of 2-amino-4H-chromene catalyzed by CuO-CeO₂ nanocomposite.

Entry	Aldehyde	Time (min)	Yield (%) ^a	M. P. (°C)	
				Found	Reported
1	C ₆ H ₅ CHO	15	94	274-275	274-276 [30]
2	3-O ₂ NC ₆ H ₄ CHO	12	93	233-235	233-235 [30]
3	4-O ₂ NC ₆ H ₄ CHO	8	92	186-188	186-187 [30]
4	2-ClC ₆ H ₄ CHO	15	94	258-260	258-260 [30]
5	4-ClC ₆ H ₄ CHO	10	90	205-207	205-206 [30]
6	2,4-Cl ₂ C ₆ H ₃ CHO	8	93	214-216	214-216 [30]
7	4-BrC ₆ H ₄ CHO	18	90	242-244	242-244 [30]
8	4-FC ₆ H ₄ CHO	12	92	234-236	233-235 [30]
9	4-MeC ₆ H ₄ CHO	18	91	271-273	270-272 [30]
10	4-MeOC ₆ H ₄ CHO	25	91	217-218	217-219 [30]
11	3,4-MeOC ₆ H ₃ CHO	45	89	209-211	210-211 [30]
12	4-HOC ₆ H ₄ CHO	40	90	247-249	246-248 [30]
13	4-Cl-3-O ₂ NC ₆ H ₃ CHO	10	91	201-203	201-202 [30]

^aYields refer to isolated and pure products.

Table 2: Recyclability study of CuO-CeO₂ nanocomposite

Run	1	2	3	4	5	6	7
Time(min)	15	15	15	18	20	20	25
Yield (%) ^a	94	93	92	92	92	92	90

^aYields refer to isolated and pure products. Reactions conditions: Benzaldehyde (1mmol), β -naphthol (1mmol), malononitrile (1mmol) and CuO-CeO₂ nanocomposite (0.05 g) under solvent-free conditions.

After reaction completion, the catalyst filtered, washed with ethyl acetate, and after dryness was reused in the next similar process. This process was repeated for 7 runs and the desired product was obtained in high yields after 1-7 runs (Table 2).

Conclusion

In conclusion, we have developed a mild, simple and efficient procedure for the one-pot synthesis of 2-amino-4*H*-chromenes using recyclable CuO-CeO₂ nanocomposite under solvent-free reaction conditions. This catalyst can promote the yields and reaction times over 7 runs without significant decrease of the catalytic activity. Moreover, ease of work-up and clean procedure, will make this method an efficient and important addition to the present methodologies for the synthesis of 2-amino-4*H*-chromenes.

Experimental

General:

All chemicals were purchased from Fluka and Merck chemical companies. All known products were characterized by comparison of their spectroscopic data (NMR, IR) and physical properties with those reported in the literature. Yields refer to isolated pure products.

Catalyst preparation:

CuO-CeO₂ nanocomposite was prepared by co-precipitation method using aqueous solution of cerium and copper nitrates and drop-wise KOH as precipitant agent under vigorous mixing while temperature and pH was fixed at unique values. Then acquired sample was filtered, washed and calcined to obtain final catalyst for using in the synthesis of 2-amino-4*H*-chromenes.

General procedure for the synthesis of 2-amino-4*H*-chromenes:

A mixture of β -naphthol (1 mmol), malononitrile (1 mmol), aldehyde (1 mmol) and CuO-CeO₂ nanocomposite (0.05 g), was heated in an oil bath (80 °C) for the appropriate times according to Table 1. After completion of the reaction (monitored by TLC), the resulting mixture was cooled, ethylacetate (10 mL) was added and the catalyst was recovered by filtration to be reused subsequently. Evaporation of the solvent from the filtrate and recrystallization of the solid residue from hot ethanol afforded the pure products in high yields. The spectral and analytical data for the known compounds are as follow:

Table 1, entry 1: IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3425, 3345, 3150, 2195, 1650, 1575, 1300, 1100, 695, 710. ¹H NMR (DMSO-d₆, 400 MHz), δ (ppm): 5.31 (S, 1H),

7.05 (S, 2H), 7.14-7.29 (m, 5H), 7.36-7.46 (m, 3H), 7.84-7.96 (m, 3H). ¹³C NMR (100 MHz, DMSO): 38.52, 58.39, 116.17, 117.27, 121.05, 124.10, 125.40, 127.09, 127.47, 127.55, 128.95, 129.19, 129.98, 130.65, 131.30, 146.21, 147.32, 160.20

Table 1, entry 3: IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3430, 3325, 2190, 1650, 1610, 1582, 1540, 1502, 1340, 1244, 1200, 1070, 810. ¹H NMR (DMSO-d₆, 400 MHz), δ (ppm): 5.45 (s, 1 H, CH), 7.20 (s, 2H), 7.36-7.52 (m, 3H), 7.69-8.03 (m, 2 H), 7.98 (d, 1 H, $J = 9.2$ Hz), 7.44 (d, 2 H), 8.15(d, 2 H). ¹³C NMR (100 MHz, DMSO): 38.53, 60.27, 116.45, 117.47, 121.17, 124.24, 125.49, 127.48, 127.62, 129.05, 129.82, 129.99, 130.74, 131.42, 136.23, 143.37, 147.33, 160.38.

Table 1, entry 7: IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3415, 3325, 3194, 3050, 2190, 1645, 1595, 1485, 1410, 1235, 1080, 1010, 825, 735. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 5.23(s, 1H), 4.64 (s, 2H), 7.07 (d, 2H, $J = 8.4$ Hz), 7.27 (d, 2H, $J = 6.3$ Hz), 7.45-7.41 (m, 3H), 7.63 (d, 1H $J = 6.4$ Hz), 7.84(d, 2H, $J = 8.5$ Hz). ¹³C NMR (100 MHz, CDCl₃): 37.82, 57.42, 115.52, 117.31, 120.21, 120.64, 124.01, 125.52, 127.72, 129.01, 129.78, 130.22, 130.52, 131.31, 132.20, 145.61, 147.31, 160.22.

Table 1, entry 9: IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3310, 3410, 3050, 2190, 1640, 1580, 1400, 1000-1300, 810. ¹H NMR (DMSO-d₆, 400 MHz), δ (ppm): 2.18 (S, 3H), 5.27 (S, 1H), 6.99 (S, 2H), 7.04-7.10 (m, 4H), 7.33 (d, 1H $J=8$ Hz), 7.39-7.46(m, 2H), 7.83 (d, 1H, $J=8.0$ Hz) 7.90-7.94 (t, 2H). ¹³C NMR (100 MHz, DMSO): 21.04, 38.22, 58.52, 116.27, 117.27, 121.06, 124.13, 125.35, 127.38, 127.51, 128.93, 129.72, 129.88, 130.66, 131.29, 136.17, 143.30, 147.24, 160.09.

Table 1, entry 11: IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3450, 3310, 2210, 1645, 1410, 1300, 1000. ¹H NMR (DMSO-d₆, 400 MHz), δ (ppm): 3.72 (s, 3H), 3.77 (s, 3H), 5.59 (s, 1H), 7.21 (s, 2H), 7.37 (d, 1H, $J=9.2$ Hz), 7.43-7.51 (m, 3H), 7.68 (d, 1H, $J=8$ Hz), 7.85 (d, 1H, $J=8.0$ Hz), 7.94-8.00 (m, 3H). ¹³C NMR (100 MHz, DMSO): 37.35, 56.45, 56.92, 57.90, 114.49, 117.39, 120.51, 123.72, 123.80, 124.21, 125.64, 127.95, 129.10, 130.30, 130.60, 131.30, 132.65, 132.86, 147.12, 147.37, 148.00, 160.41.

Table 1, entry 13: IR (KBr) $\nu_{\max}/\text{cm}^{-1}$: 3415, 3305, 2210, 1650, 1555, 1350, 1300, 1010, 800, 745. ¹H NMR (DMSO-d₆, 400 MHz), δ (ppm) 5.57(s, 1H), 7.21(s, 2H), 7.34(d, 1H, $J=9.2$ Hz), 7.43-7.51(m, 3H), 7.69(d, 1H, $J=8$ Hz), 7.84 (d, 1H, $J=8.0$ Hz), 7.94-8.00 (m, 3H). ¹³C NMR (100 MHz, DMSO): δ (ppm): 37.37, 56.96, 114.52, 11.41, 120.54, 123.77, 123.84, 124.24, 125.67, 127.97, 129.12, 130.34, 130.65,

131.36, 132.69, 132.92, 147.17, 147.42, 148.03, 160.46.

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