

Research Article

CuO-CeO₂ Nanocomposite: An Efficient Recyclable Catalyst for the Synthesis of Aryl-14*H*-dibenzo[a-j]xanthenes

Jalal Albadi,¹ Abdolhossein Razeghi,² Hossein Abbaszadeh,³ and Azam Mansournezhad³

¹ College of Science, Behbahan Khatam Alanbia University of Technology, Behbahan 736254, Iran

² Catalysis and Reaction Engineering, Tehran University, Tehran, Iran

³ Department of Chemistry, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran

Correspondence should be addressed to Jalal Albadi; jalal.albadi@gmail.com

Received 7 January 2013; Revised 16 February 2013; Accepted 20 February 2013

Academic Editor: Hamed Bahmanpour

Copyright © 2013 Jalal Albadi et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

CuO-CeO₂ nanocomposite is reported as a highly efficient recyclable catalyst that is applied for the synthesis of Aryl-14*H*-dibenzo[a-j]xanthenes under solvent-free conditions. The catalyst was synthesized by coprecipitation method and characterized by X-ray powder diffraction (XRD), BET specific surface area, field emission scanning electron microscopy (FESEM), and energy dispersive spectroscopy (EDS) analysis. The copper nanoparticles are dispersed as fine and amorphous phases on the surface of ceria and made nanoclusters with average size of about 33 nm. This catalyst can be recovered by simple filtration and recycled up to 8 consecutive runs without any losing of its efficiency. This procedure provides several advantages such as simple workup, mild reaction conditions, short reaction times, and high yields of the products.

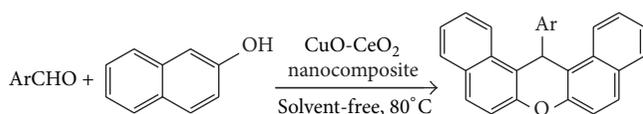
1. Introduction

In recent years, nanocatalysis has emerged as a sustainable and competitive alternative to conventional catalyst since the nanoparticles possess a high-surface-to-volume ratio, which enhances their activity and selectivity, while, at the same time, maintaining the intrinsic features of a heterogeneous catalyst [1]. In particular, nanocrystalline oxides have proved to be useful to chemists in the laboratory and industry due to the good activation of adsorbed compounds and reaction rate enhancement, selectivity, easier workup and recyclability of the supports, and the eco-friendly green reaction conditions [2–6]. Also, the practical applications of nanocomposite metal oxides as the catalysts in organic synthesis have been increased due to their high catalytic activity because of the high surface area [7, 8]. The recyclability of the catalyst is the added advantage in the case of these catalysts. The catalytic activity of CuO-CeO₂ nanocomposite is well known for the oxidation of CO in H₂-rich streams [9]. Xanthene derivatives are important class of compounds that received significant attention from many pharmaceutical and organic chemists because of the broad spectrum of their biological and pharmaceutical properties such as antibacterial [10],

anti-inflammatory [11], and antiviral properties [12]. Furthermore, these compounds are used as dyes and fluorescent material for visualization of biomolecules and in laser technologies due to their useful spectroscopic properties [13, 14]. Aryl-14*H*-dibenzo[a-j]xanthenes are among the most important classes in the family of xanthenes due to their distinctive structures and great potential for the further transformations [15]. Various methods have been reported for the synthesis of Aryl-14*H*-dibenzo[a-j]xanthenes; among these methods, the one-pot condensation of β -naphthol with aldehydes is the most common procedure. Therefore, various catalysts have been developed for the improvement of this reaction [16–25]. In the continuation of our research program to develop the efficient, and green catalysts in organic synthesis [26–29], herein, we wish to report a green, efficient and recyclable catalyst for the synthesis of Aryl-14*H*-dibenzo[a-j]xanthenes under solvent-free conditions (Scheme 1).

2. Experimental

All products were identified by the comparison of their spectral and physical data with authentic samples. Chemicals (2-naphthol, aromatic aldehydes, cerium, and copper nitrates)



SCHEME 1: Synthesis of Aryl-14H-dibenzo[a-j]xanthenes catalyzed by CuO-CeO₂ nanocomposite oxide.

were purchased from Merck Chemical company in Germany. Yields refer to isolated pure products.

2.1. Catalyst Preparation. CuO-CeO₂ nanocomposite was prepared by coprecipitation method using aqueous solution of cerium and copper nitrates and drop-wise adding KOH as precipitant agent under vigorous mixing, while temperature and pH were fixed at unique values. Then, acquired sample was filtered, washed, and calcined to obtain final catalyst for using at synthesis of Aryl-14H-dibenzo[a-j]xanthenes.

2.2. General Procedure for Synthesis of Aryl-14H-dibenzo[a-j]xanthenes. A mixture of 2-naphthol (2 mmol), aldehyde (1 mmol), and CuO-CeO₂ nanocomposite (0.05 g) was added to a round-bottomed flask. The reaction mixture was placed in an oil bath at 80°C and magnetically stirred for the appropriate times according to Table 1. After completion of the reaction (monitored by TLC), the mixture reaction was cooled to room temperature, next acetone (10 mL) was added, and the mixture stirred for 5 min. Then, the catalyst was recovered by filtration to be reused subsequently. The filtrate was evaporated to dryness, and the solid residue recrystallized from hot ethanol to give pure products in high yields. The experimental procedure with this catalyst is very simple and the catalyst can be removed easily by filtration. The solid products were easily recrystallized from hot ethanol and were obtained in good to high yields during the short reaction times. Very low amount of the catalyst is needed. Moreover, our procedure is environmentally friendly as it does not use any toxic auxiliary or solvent.

2.3. Catalyst Characterization. The catalyst structure characterization was performed by X-ray powder diffraction (XRD), using a Bruker AXS D8 advanced diffractometer equipment with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). The Debye-Scherrer equation is used to determine average crystallite size of nanoparticles. Field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS) carried out by a Hitachi S4160 instrument to see the morphology, the evaluation of cluster size, and the metal composition of the catalyst. BET specific surface area was estimated from the N₂ adsorption/desorption isotherms, measured at 77°K using a Quantachrome CHEMBET-3000 instrument.

3. Results and Discussions

XRD pattern of fresh CuO-CeO₂ nanocomposite calcined at 450°C is illustrated (Figure 1). The main reflection placed at 2θ range of 15–80° indicates a cubic fluorite structure

TABLE 1: Synthesis of Aryl-14H-dibenzo[a-j]xanthenes catalyzed by CuO-CeO₂ nanocomposite.

Entry	Aldehyde	Time (min)	Yield (%) ^a	M. P. (°C)
1	PhCHO	15	93	185–186
2	2-NO ₂ C ₆ H ₄ CHO	12	91	213–215
3	3-NO ₂ C ₆ H ₄ CHO	15	90	210–211
4	4-NO ₂ C ₆ H ₄ CHO	8	90	310–312
5	2-ClC ₆ H ₄ CHO	12	90	213–215
6	4-ClC ₆ H ₄ CHO	10	91	289–290
7	2,4-Cl ₂ C ₆ H ₃ CHO	12	90	251–252
8	2,6-Cl ₂ C ₆ H ₃ CHO	15	89	267–269
9	4-FC ₆ H ₄ CHO	10	90	237–238
10	2-MeC ₆ H ₄ CHO	18	89	258–260
11	3-MeC ₆ H ₄ CHO	12	90	199–201
12	4-MeC ₆ H ₄ CHO	20	90	228–229
13	4-MeOC ₆ H ₄ CHO	30	89	202–204
14	4-BrC ₆ H ₄ CHO	15	91	296–298
15	4-OHC ₆ H ₄ CHO	45	88	139–141

^a Isolated yield. ^b Products were characterized by the comparison of their spectroscopic data (NMR and IR) and melting points with those reported in the literature [17, 18].

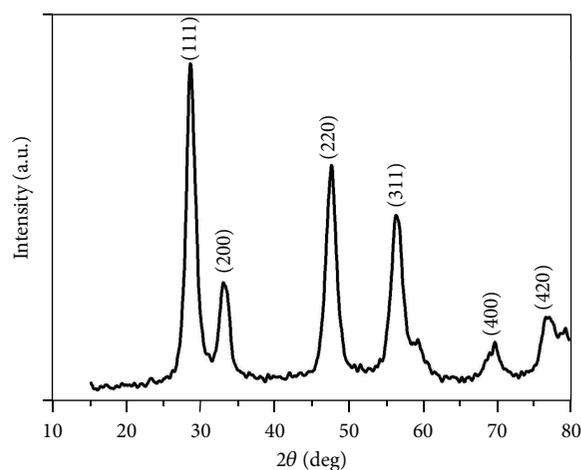
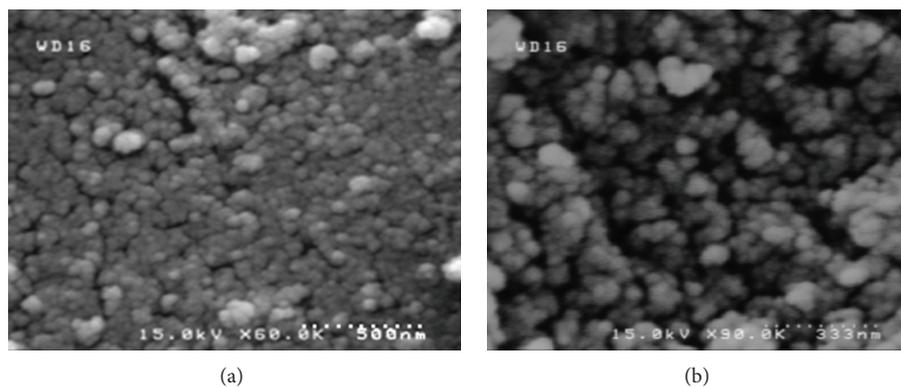
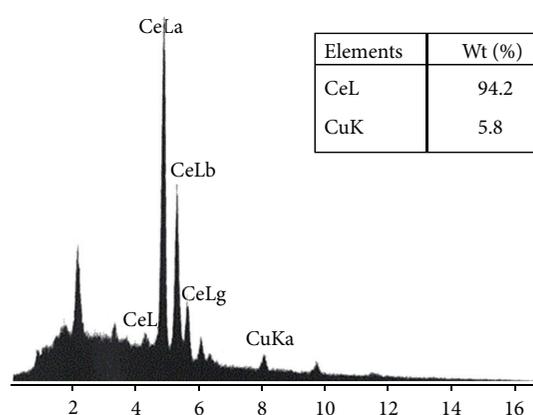


FIGURE 1: XRD pattern of the CuO-CeO₂ nanocomposite catalyst.

with highest intensity at (1, 1, 1) plane that belongs to the XRD standard JCPDS card number of 43-1002. According to the pattern of pure CeO₂ (not shown in the figure), only the diffraction peaks of ceria crystallites are detected, and there is no peaks related to copper oxide nanoparticles. It is supposed that fine dispersion and/or amorphous structure of CuO with low content on the surface of ceria clusters is responsible for absence of copper oxide peaks at the XRD pattern [9, 30, 31]. However, there is some difference between values of unit cell parameters for pure CeO₂ and CuO-CeO₂ due to lattice shrinkage in surface ceria structure. The calculation showed 5.45 and 5.42° Å for CeO₂ and CuO-CeO₂, respectively. The observed shrinkage may be consequence of partial incorporation of CuO into the CeO₂ lattice structure that has been reported for coprecipitation synthesis [30, 31]. The calculated average crystal size of the ceria in the

FIGURE 2: FESEM image of the CuO-CeO₂ nanocomposite catalyst.FIGURE 3: EDS analysis of the CuO-CeO₂ nanocomposite catalyst.

catalyst based on dominant peak at 2θ of 28.5° using Debye-Scherrer equation was 7.5 nm. BET specific surface area result was $131 \text{ m}^2/\text{g}$ that confirms estimated value for average nanoparticle size of the catalyst by XRD test.

Figures 2(a) and 2(b) present FESEM micrograph of the catalyst at two different magnifications to study the morphology and the evaluation of nanoclusters size of catalyst. It seems that 7 nm particles calculated based on the BET surface area are agglomerated to approximately 33 nm sized clusters and made bigger nanostructure CuO-CeO₂ catalyst.

EDS analysis (Figure 3) showed the presence of 5.8 and 94.2 wt.% for Cu and Ce elements in the catalyst, respectively.

Optimization of the reaction conditions showed that the best results in the presence of 0.05 g of CuO-CeO₂ nanostructured catalyst at 80°C were obtained under solvent-free conditions, when the relative ratio of the aldehyde and 2-naphthol was 2 : 1, respectively. Using these optimized conditions, the reaction of various aromatic aldehydes, containing electron-donating and electron-withdrawing groups, was explored (Table 1). Aliphatic aldehydes remain intact under the same reaction conditions. Therefore, the method can be useful for the chemoselective synthesis of Aryl-14H-dibenzo[a-j]xanthenes from aromatic aldehydes in the presence of aliphatic ones.

TABLE 2: Recyclability of CuO-CeO₂ nanocomposite.

Run	1	2	3	4	5	6	7	8
Time (min)	15	15	15	18	18	20	20	25
Yield (%) ^a	93	93	92	92	92	90	88	88

^a Isolated yield.

The activity of the recycle catalyst was also examined under the optimized conditions, and the desired product was obtained in high yields after 1–8 runs (Table 2). To investigate these property for our introduced catalyst, the reaction of benzaldehyde with 2-naphthol was selected as the model (Table 2). After each reaction, we washed and dried the catalyst with acetone and reused for the next run. This process was repeated for 8 runs, and no appreciable yield decrease was observed.

4. Conclusions

We have developed a new, efficient, and green procedure for the synthesis of biologically important xanthene derivatives catalyzed by recyclable CuO-CeO₂ nanostructured catalyst, under solvent-free conditions. This catalyst can promote the yields and reaction times over 8 runs without noticeable loss in its efficiency. Moreover, high yields of products, short reaction times, ease of workup, and clean operation are the most important advantages of this method which makes the procedure beneficial compared to conventional methods.

Acknowledgment

The authors are thankful to the Behbahan Khatam Al-Anbia, University of Technology, for the partial support of this work.

References

- [1] D. Astruc, *Nanoparticles and Catalysis*, Wiley-VCH, Weinheim, Germany, 2008.
- [2] H. Sharghi and M. Hosseini, "Solvent-free and one-step Beckmann rearrangement of ketones and aldehydes by zinc oxide," *Synthesis*, no. 8, pp. 1057–1059, 2002.

- [3] M. H. Sarvari and H. Sharghi, "Reactions on a solid surface. A simple, economical and efficient Friedel-Crafts acylation reaction over zinc oxide (ZnO) as a new catalyst," *Journal of Organic Chemistry*, vol. 69, no. 20, pp. 6953–6956, 2004.
- [4] S. F. Yin, B. Q. Xu, S. J. Wang, C. F. Ng, and C. T. Au, "Magnesia-Carbon nanotubes (MgO-CNTs) nanocomposite: novel support of Ru Catalyst for the generation of CO_x-free Hydrogen from Ammonia," *Catalysis Letters*, vol. 96, pp. 113–116, 2004.
- [5] M. T. Drexler and M. D. Amiridis, "Kinetic investigation of the heterogeneous synthesis of flavanone over MgO," *Catalysis Letters*, vol. 79, no. 1–4, pp. 175–181, 2002.
- [6] R. S. Varma, "Solvent-free organic syntheses: using supported reagents and microwave irradiation," *Green Chemistry*, vol. 1, no. 1, pp. 43–55, 1999.
- [7] S. Samantaray, D. K. Pradhan, G. Hota, and B. G. Mishra, "Catalytic application of CeO₂-CaO nanocomposite oxide synthesized using amorphous citrate process toward the aqueous phase one pot synthesis of 2-amino-2-chromenes," *Chemical Engineering Journal*, vol. 193, pp. 1–9, 2012.
- [8] S. Li, W. Zhang, M. H. So, C. M. Che, R. Wang, and R. Chen, "One-pot solvothermal synthesis of Pd/F_e₃O₄ nanocomposite and its magnetically recyclable and efficient catalysis for Suzuki reactions," *Journal of Molecular Catalysis A*, vol. 359, pp. 81–87, 2012.
- [9] A. Razeghi, A. Khodadadi, H. Ziaei-Azad, and Y. Mortazavi, "Activity enhancement of Cu-doped ceria by reductive regeneration of CuO-CeO₂ catalyst for preferential oxidation of CO in H₂-rich streams," *Chemical Engineering Journal*, vol. 164, no. 1, pp. 214–220, 2010.
- [10] S. Chatterjee, M. Iqbal, J. C. Kauer et al., "Xanthene derived potent nonpeptidic inhibitors of recombinant human calpain I," *Bioorganic and Medicinal Chemistry Letters*, vol. 6, no. 13, pp. 1619–1622, 1996.
- [11] J. P. Poupelin, G. Saint Ruf, O. Foussard Blanpin, G. Narcisse, G. Uchida-Ernouf, and R. Lacroix, "Synthesis and antiinflammatory properties of bis (2 hydroxy 1 naphthyl) methane derivatives," *European Journal of Medicinal Chemistry*, vol. 13, no. 1, pp. 67–71, 1978.
- [12] O. Sirkecioglu, N. Tulinli, and A. Akar, "Synthesis of 14-Aryl-14H-dibenzo[a-j]xanthenes," *Journal of Chemical Research*, pp. 502–506, 1995.
- [13] R. M. Ion, A. Planner, K. Wiktorowicz, and D. Frackowiak, "The incorporation of various porphyrins into blood cells measured via flow cytometry, absorption and emission spectroscopy," *Acta Biochimica Polonica*, vol. 45, no. 3, pp. 833–845, 1998.
- [14] R. J. Sarma and J. B. Baruah, "One step synthesis of dibenzoxanthenes," *Dyes and Pigments*, vol. 64, no. 1, pp. 91–92, 2005.
- [15] K. Chibale, M. Visser, D. Van Schalkwyk, P. J. Smith, A. Saravanamuthu, and A. H. Fairlamb, "Exploring the potential of xanthene derivatives as trypanothione reductase inhibitors and chloroquine potentiating agents," *Tetrahedron*, vol. 59, no. 13, pp. 2289–2296, 2003.
- [16] L. Wu, J. Zhang, L. Fang, C. Yang, and F. Yan, "Silica chloride catalyzed synthesis of 14-aryl-14H-dibenzo[a,i]xanthene-8,13-diones," *Dyes and Pigments*, vol. 86, no. 1, pp. 93–96, 2010.
- [17] S. Allameh, A. Davoodnia, and A. Khojastehnezhad, "An efficient and eco-friendly synthesis of 14-Aryl-14H-dibenzo[a-j]xanthenes using H₄[SiW₁₂O₄₀] as a heterogeneous and reusable catalyst under solvent-free conditions," *Chinese Chemical Letters*, vol. 23, pp. 17–20, 2012.
- [18] I. Mohammadpoor-Baltork, M. Moghadam, V. Mirkhani, S. Tangestaninejad, and H. R. Tavakoli, "Highly efficient and green synthesis of 14-aryl(alkyl)-14H-dibenzo[a,j] xanthene and 1,8-dioxooctahydroxanthene derivatives catalyzed by reusable zirconyl triflate [ZrO(OTf)₂] under solvent-free conditions," *Chinese Chemical Letters*, vol. 22, no. 1, pp. 9–12, 2011.
- [19] A. R. Hajipour, Y. Ghayeb, N. Sheikhan, and A. E. Ruoho, "Brønsted acidic ionic liquid as an efficient and reusable catalyst for synthesis of 14-aryl- or 14-Aryl-14H-dibenzo[a-j]xanthenes under solvent-free conditions," *Synlett*, no. 5, pp. 741–744, 2010.
- [20] S. Ko and C. F. Yao, "Heterogeneous catalyst: amberlyst-15 catalyzes the synthesis of 14-substituted-14H-dibenzo[a,j] xanthenes under solvent-free conditions," *Tetrahedron Letters*, vol. 47, no. 50, pp. 8827–8829, 2006.
- [21] T. S. Rivera, A. Sosa, G. P. Romanelli, M. N. Blanco, and L. R. Pizzio, "Tungstophosphoric acid/zirconia composites prepared by the sol-gel method: an efficient and recyclable green catalyst for the one-pot synthesis of 14-Aryl-14H-dibenzo[a-j]xanthenes," *Applied Catalysis A*, vol. 443, pp. 207–213, 2012.
- [22] M. Dabiri, M. Baghbanzadeh, M. Shakouri Nikcheh, and E. Arzroomchilar, "Eco-friendly and efficient one-pot synthesis of alkyl- or Aryl-14H-dibenzo[a-j]xanthenes in water," *Bioorganic and Medicinal Chemistry Letters*, vol. 18, no. 1, pp. 436–438, 2008.
- [23] G. B. Dharma Rao, M. P. Kaushik, and A. K. Halve, "An efficient synthesis of naphtha[1, 2-e]oxazinone and 14-substituted-14H-dibenzo [a, j] xanthene derivatives promoted by zinc oxide nanoparticle under thermal and solvent-free conditions," *Tetrahedron Letters*, vol. 53, pp. 2741–2744, 2012.
- [24] F. Shirini and N. Ghaffari Khaligh, "Succinimide-N-sulfonic acid: an efficient catalyst for the synthesis of xanthene derivatives under solvent-free conditions," *Dyes and Pigments*, vol. 95, pp. 789–794, 2012.
- [25] R. Kumar, G. C. Nandi, R. K. Verma, and M. S. Singh, "A facile approach for the synthesis of 14-aryl- or alkyl-14H-dibenzo[a,j]xanthenes under solvent-free condition," *Tetrahedron Letters*, vol. 51, no. 2, pp. 442–445, 2010.
- [26] J. Albadi, M. Keshavarz, F. Shirini, and M. Vafaie-nezhad, "Copper iodide nanoparticles on poly(4-vinyl pyridine): a new and efficient catalyst for multicomponent click synthesis of 1,4-disubstituted-1,2,3-triazoles in water," *Catalysis Communications*, vol. 27, pp. 17–20, 2012.
- [27] J. Albadi, N. Iravani, F. Shirini, and F. Dehghan, "A green recyclable poly(4-vinylpyridine)-supported copper iodide nanoparticle catalyst for the chemoselective synthesis of pentaerythritol diacetals from aromatic aldehydes," *Journal of Chemical Research*, vol. 36, no. 10, pp. 610–611, 2012.
- [28] J. Albadi, N. Iravani, and M. Khoshakhlagh, "A new, green and recyclable poly(4-vinylpyridine)-supported copper iodide nanoparticles catalyst for the synthesis of aryl -14H-dibenzo[a-o]xanthenes," *Iranian Journal of Catalysis*, vol. 2, pp. 85–89, 2012.
- [29] J. Albadi, M. Keshavarz, M. Abedini, and M. Vafaie-nezhad, "Copper iodide nanoparticles on poly(4-vinyl pyridine) as new and green catalyst for multicomponent click synthesis of 1, 4-disubstituted-1, 2, 3-triazoles in water," *Chinese Chemical Letters*, vol. 23, pp. 797–800, 2012.
- [30] P. Ratnasamy, D. Srinivas, C. V. V. Satyanarayana et al., "Influence of the support on the preferential oxidation of CO in hydrogen-rich steam reformates over the CuO-CeO₂-ZrO₂ system," *Journal of Catalysis*, vol. 221, pp. 455–465, 2004.

- [31] Z. Liu, R. Zhou, and X. Zheng, "Preferential oxidation of CO in excess hydrogen over a nanostructured CuO-CeO₂ catalyst with high surface areas," *Catalysis Communications*, vol. 9, pp. 2183–2186, 2008.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

