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A new, green and recyclable poly(4-vinylpyridine)-supported copper iodide nanoparticles catalyst for the synthesis of aryl-14*H*-dibenzo [a-o] xanthenes

Jalal Albadi[a*], Nasir Iravani[b], Moloud Khoshakhlagh[b]

[a]*College of Science, Behbahan Khatam Alanbia University of Technologhy, Behbahan, Iran*
[b]*Department of Chemistry, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran*

ABSTRACT

Poly(4-vinylpyridine)-supported copper iodide nanoparticles is reported as a new, green and recyclable catalyst for the synthesis of aryl-14*H*-dibenzo [a-o] xanthenes under solvent-free conditions. This catalyst can be recovered by simple filtration and recycled up to 8 consecutive runs without any loss of their efficiency.

Keywords: *Poly(4-vinylpyridine)-Supported, β-naphthol, aryl-14H-dibenzo [a-o] xanthenes, Nanoparticles, Copper catalysis, Solvent-free conditions .*

1. Introduction

Xanthenes and benzoxanthenes 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[1], anti-inflammatory [2], and antiviral properties [3] . Furthermore, these compounds are used as dyes, fluorescent material for visualization of biomolecules and in laser technologies due to their useful spectroscopic properties [4]. Aryl-14*H*-dibenzo [a-o] xanthenes are among the most important classes in the family of xanthenes due to their distinctive structures and great potential for the further transformations. Various methods have been reported for the synthesis of aryl-14H-dibenzo [a-o] xanthenes [5-8], which of them 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 [9-19]. Recently CuI is emerging as an effective Lewis acid catalyst for the various organic transformations [20-24]. However, CuI have some limitations such as thermodynamic instability, long reaction times, non-recyclable, toxicity and difficulty in separation of the product from the reaction mixture. Such drawbacks could be obviated by using the supported catalyst. Nitrogen-based polymer have been shown to protect the metal center

from oxidation and disproportionation, while enhancing its catalytic activity [25]. To improve the recovery and reuse, copper species have been immobilized on various supports such as carbon [26], amine-functionalized polymers [27], zeolites [28], amine-functionalized silica [29] and aluminum oxyhydroxide fiber [30]. In particular, the immobilization of copper(I) salts nanoparticles (CuNPs) on supports with high surface area allows a higher stability and dispersity of the particles as well as a further exploitation of the special activity and recycling properties of the catalyst. In the recent years, nano catalyst 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 [31]. Poly(4-vinylpyridine)-supported reagents are active for the various organic reactions including oxidations, reductions and halogenations. Simple recovery from reaction mixtures, their reusability, and compatibility with a wide range of solvents, physical stability, and their toleration of a great number of reaction conditions bode well for the future of P_4VPy-supported reagents in which their properties can be fine-tuned for specific chemical transformations [32]. Recently, we have reported the preparation of the poly(4-vinylpyridine)-supported copper iodide nano particles catalyst (P_4VPy-CuI) and its application for the click synthesis of triazole derivatives. [33-34]. In continuation of these studies, herein, we wish to report the applicability of this reagent for the synthesis of aryl-14*H*-dibenzo [a-o] xanthenes under solvent-free conditions (Scheme 1).

* Corresponding author: E-mail: Chemalbadi@gmail.com.
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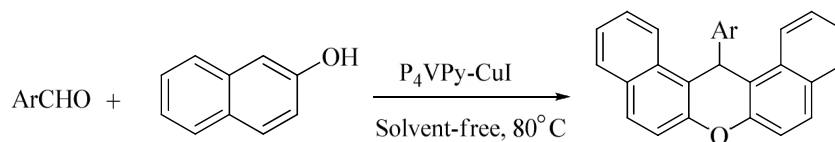
Scheme 1. Synthesis of aryl-14*H*-dibenzo [a-o] xanthenes catalyzed by P₄VPy-CuI.

2. Experimental

All products were identified by comparison of their spectral and physical data with authentic samples. Chemicals were purchased from Fluka, Merck and Aldrich Chemical companies. Yields refer to isolated pure products.

2.1. Preparation of the polymer supported catalyst

CuI (0.381 g) was put in 30 mL ethanol, and magnetically stirred at reflux temperature for 4 h under nitrogen atmosphere in the presence of dry poly(4-vinylpyridine) (1.0 g, mesh 50-60). The solvent was filtered, the resin washed with CH₃CN (2×20 mL) and dried under vacuum at 60 ° C overnight. The weight increase was 0.31 g (1.63 mmol CuI), which gave a polymer loading of 1.24 mmol CuI.g⁻¹. The exact copper content of poly(4-vinylpyridine)-CuI was measured using ICP-AES. The loading of supported catalyst was calculated to be 1.32 mmol CuI.g⁻¹ of resin. Scanning electron microscopy (SEM), X-ray diffraction (XRD), atomic absorption and IR experimental techniques were used to characterize the catalyst.

2.2. Determination of the copper content in P_4VPy-CuI

The P₄VPy-CuI (100 mg) was extracted with concentrated HCl (5×2 mL) in a screw-capped vessel, followed by treatment with concentrated nitric acid (2 mL) to digest the metal complex. The mixture was then transferred into a volumetric flask (100 mL), diluted 1:50 for the second time and was analyzed by the ICP analysis. The copper concentration was determined from the atomic emissions (324.754 nm) by reference to a linear (R=0.99) calibration curve of (1–4 ppm) of CuI prepared in a manner identical to the sample preparation. The loading of supported catalyst was calculated to be 1.32 mmol CuI.g⁻¹ of prepared catalyst. The same procedure was used to measure the leaching accounts of supported catalyst after 8 consecutive runs.

2.3. General procedure for the synthesis of aryl-14H-dibenzo [a-o] xanthenes

A mixture of *β*-naphthol (2 mmol), aldehyde (1 mmol) and P4VPy-CuI (0.1 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 reaction was cooled to room temperature, acetone (10 mL) was added and the mixture stirred for 5 min.Then 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 (IR, ¹HNMR) data for the selected compounds are presented below.

The selected spectral data

Table 1, entry 1: IR (KBr, cm⁻¹): 3075, 3022, 2885, 1620, 1591, 1512, 1489, 1457, 1402, 1253, 1079, 1026, 964, 827, 744, 700. ¹H NMR (500 MHz, DMSO-d₆, ppm) δ: 6.53 (1H, s), 7.04 (1H, t, *J* = 7.4 Hz), 7.19 (2H, t, *J* = 7.6 Hz), 7.45 (2H, t, *J* = 7.0 Hz), 7.54 (2H, d, *J* = 8.9 Hz,), 7.58 (2H, d, *J* = 7.3 Hz), 7.62 (2H, t, *J* = 7.0), 7.83 (d, 2H, *J* = 8.9 Hz), 7.87 (d, 2H, *J* = 8.0 Hz), 8.44 (d, 2H, *J* = 8.5 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm) δ: 38, 116.6, 118.5, 123, 124.5, 126.5, 127, 128.7, 128.9, 129, 129.2, 131.2, 131.5, 145.2, 148.7.

Table 1, entry 3: IR (KBr, cm⁻¹): 3075, 2890, 1640, 1565, 1487, 1457, 1345, 1250, 1052, 1055. ¹H NMR (500 MHz, DMSO-d₆, ppm) δ: 6.62 (1H, s), 7.32 (1H, t, *J* = 8.0 Hz), 7.47 (2H, t, *J* = 7.4 Hz), 7.55 (2H, d, *J* = 8.9 Hz), 7.65 (2H, t, *J* = 7.4 Hz), 7.82-7.91 (m, 6H,), 7.33 (2H, d, *J* = 8.5 Hz), 8.42 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ: 37.8, 116.2, 118.4, 121.8, 122.5, 122.9, 125.4, 127.7, 129.1, 129.6, 129.8, 131.2, 134.6, 147.2, 148.4, 148.8.

Table 1, entry 5: IR (KBr, cm⁻¹): 3095, 3020, 2890, 1640, 1590, 1487, 1457, 1325, 1250, 1082, 1045. ¹H NMR (500 MHz, DMSO-d₆, ppm) δ: 6.53 (1H, s), 7.12 (2H, t, *J* = 8.5 Hz, Ar–H), 7.42-7.51 (4H, m), 7.55 (2H, d, *J* = 8.9 Hz), 7.62 (2H, t, *J* = 7.4 Hz), 7.82 (2H, d, *J* = 8.9 Hz), 7.87 (2H, d, *J* = 8 Hz), 8.39 (2H, d, *J* = 8.5 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm) δ: 36.5, 117.7, 117.9, 124.2, 125.5, 127.9, 129.2, 129.5, 130.1, 130.5, 131.5, 131.6, 132.1, 145.3, 148.7.

Table 1, entry 10: IR (KBr, cm⁻¹): 3090, 3025, 2890, 1640, 1590, 1487, 1325, 1250, 1085, 1050. ¹H NMR (500 MHz, DMSO-d₆, ppm) δ: 2.4 (s, 3H, CH₃), 6.63 (s, 1H), 6.91 (2H, d, *J* = 8.0 Hz), 7.46 (2H, t, *J* = 7.4 Hz), 7.51 (2H, d, *J* = 8.1 Hz), 7.56 (2H, d, *J* = 8.8 Hz), 7.61 (2H, t, J = 7.2 Hz), 7.91(2H, d, J = 8.9 Hz), 7.92 (2H, d, *J* = 7.7 Hz), 8.65 (2H, d, *J* = 8.5 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm) δ: 20.2, 37.2, 116.5, 116.9, 117.8, 123.9, 124.7, 126.2, 127.3, 128.7, 129.1, 131.2, 135.9, 142.5, 147.9, 148.2.

3. Results and Discussion

The copper(I) iodid catalyst immobilized on poly(4-vinylpyridine) was readily prepared in a one-step procedure. Poly(4-vinylpyridine) was refluxed with a solution of CuI under N₂ atmosphere in EtOH for the synthesis of polymer-supported CuI nanoparticles. This method was developed
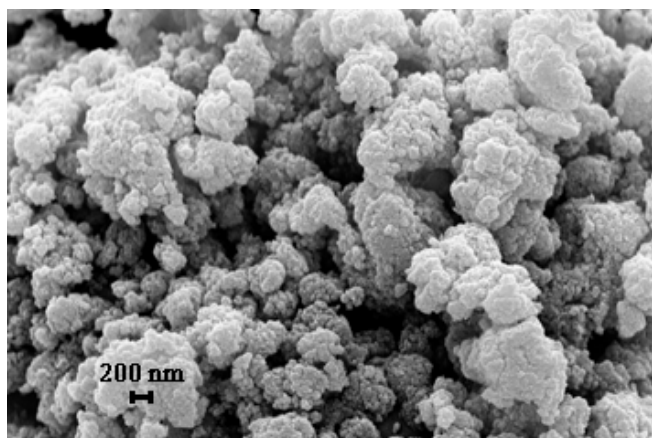
Fig. 1. SEM image of poly(4-vinyl pyridine)-supported CuI nano particles

for the effective synthesis of copper nanoparticles incorporated heterogeneously as a catalyst in some organic reactions [35]. Scanning electron microscopy (SEM) (Fig. 1), X-ray diffraction (XRD) (Fig. 2), FT-IR experimental techniques (Fig. 3) and ICP analysis techniques were used to characterize the catalyst. The SEM image of the prepared catalyst indicated that CuI nanoparticles were homogeneously immobilized on poly(4-vinylpyridine) surface. According to the SEM images of P_4VPy-CuI, the average size of copper nanoparticles was estimated to be 75-100 nm. The sharp peaks were observed in the XRD patterns of P_4VPy-CuI and their positions were consistent with metallic copper and copper iodide nanocrystals. The size of copper nanoparticles was also determined from X-ray line broading using the Debye–Scherrer formula (obtained size: 75 nm). The weak absorption band around

667 cm^{-1} were observed in the FT-IR spectra related to the immobilization of copper iodide nanoparticles on poly (4-vinylpyridine) surface. To optimize the reaction conditions, the reaction of benzaldehyde and 2-naphthol was investigated as a model and its behavior was studied under a variety of conditions. The best result was achieved by carrying out the reaction of benzaldehyde and 2-naphthol (with 1: 2 mol ratios) in the presence of 0.1 g of P_4VPy-CuI at 80 $^\circ$C (Table 1, entry 1). Using these optimized conditions, the reaction of various aromatic aldehydes, containing electron-donating and electron-withdrawing groups, was explored. Aliphatic aldehydes remain intact under the same reaction conditions. Therefore, the method can be useful for the chemoselective synthesis of aryl-14*H*-dibenzo [a-o] xanthenes from aromatic aldehydes in the presence of aliphatic ones. All the products were cleanly

Table 1. Synthesis of 14-aryl-14*H*-dibenzo[a-o]xanthene catalyzed by P_4VPy-CuI.

| Entry	Aldehyde	Time (min)	Yield (%)[a]	m.p. ($^\circ$C)	
				Found	Reported
1	PhCHO	22	92	184-186	183-185[12]
2	2-NO$_2$C$_6$H$_4$CHO	18	90	213-215	214-215[13]
3	3-NO$_2$C$_6$H$_4$CHO	15	90	210-211	210-212[12]
4	4-NO$_2$C$_6$H$_4$CHO	10	92	311-313	310-313[12]
5	2-ClC$_6$H$_4$CHO	15	90	213-215	214-216[13]
6	4-ClC$_6$H$_4$CHO	12	92	289-291	290-291[12]
7	4-FC$_6$H$_4$CHO	12	89	237-239	238-240[12]
8	2-MeC$_6$H$_4$CHO	25	92	258-260	257-258[13]
9	3-MeC$_6$H$_4$CHO	20	90	199-200	198-200[13]
10	4-MeC$_6$H$_4$CHO	30	93	227-229	228-230[12]
11	2-MeOC$_6$H$_4$CHO	20	89	204-206	203-205[13]
12	4-MeOC$_6$H$_4$CHO	45	88	202-204	222-205[12]
13	4-BrC$_6$H$_4$CHO	18	92	296-298	296-298[12]
14	3-OHC$_6$H$_4$CHO	30	90	244-246	243-245[12]
15	4-OHC$_6$H$_4$CHO	60	89	139-141	138-140[12]
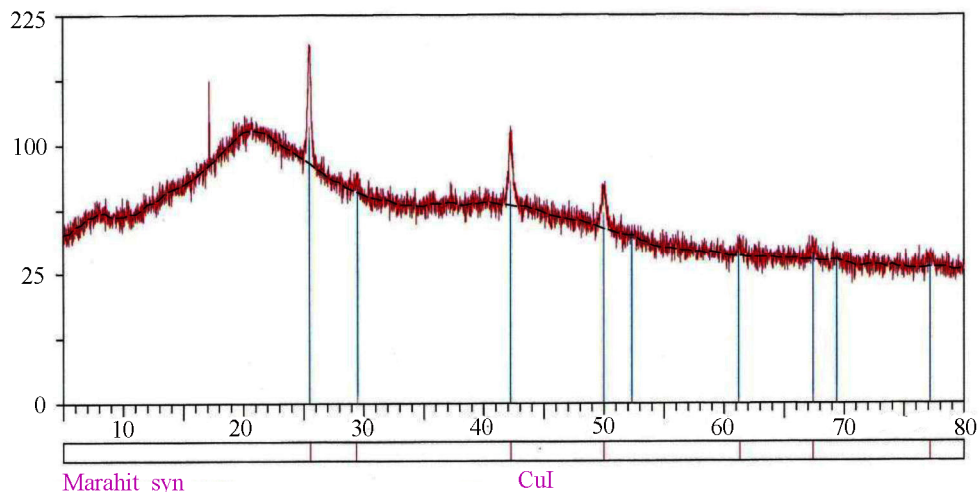
Fig. 2. XRD pattern of poly(4-vinyl pyridine)-supported CuI nano particles.
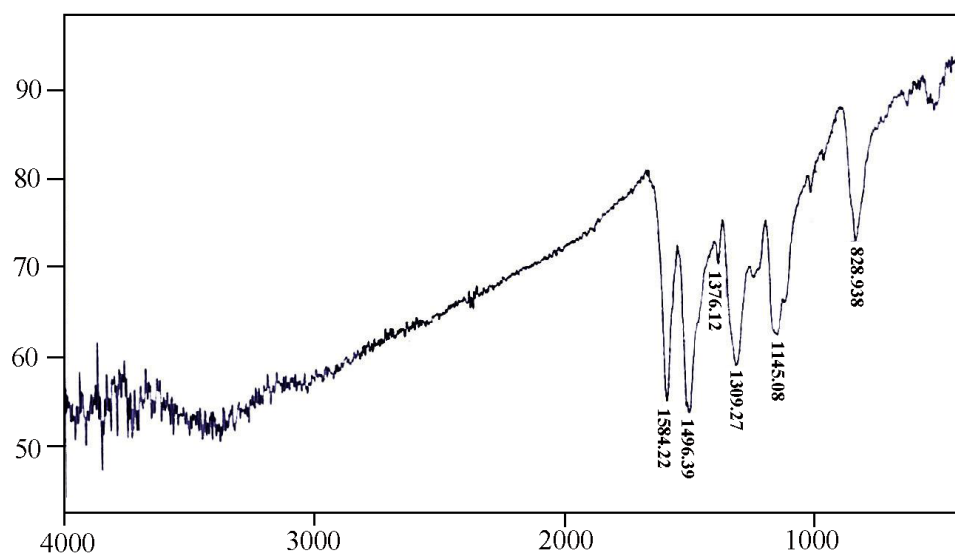

Fig. 3. FT-IR spectra of poly(4-vinyl pyridine)-supported CuI nano particles.

isolated with simple filtration and evaporation of solvent. The solid products were easily recrystallized from hot ethanol and were obtained in good to high yields during short reaction times. The activity of the recovered catalyst was also examined under the optimized conditions. To investigate these property for our introduced catalyst, the reaction of benzaldehyde with 2-naphthol was selected as the model (Table 2). After reaction completion, P_4VPy-CuI was washed with ethylacetate, dried and stored for another consecutive reaction run. This process was repeated for 8 runs and no appreciable yield decrease was observed. It is also noteworthy that P_4VPy-CuI does not suffer from extensive mechanical degradation after running. Next we checked the leaching of CuI into the reaction mixture from the poly(4-vinylpyridine) support using ICP-AES. The difference between the copper content of the fresh and

reused catalyst (8th run) is only 2% which indicates the low leaching amount of copper iodide catalyst into the reaction mixture.

4. Conclusion

In conclusion, we have developed a new, efficient and green procedure for the synthesis of biologically important xanthene derivatives catalyzed by recyclable P_4VPy–CuI, under solvent-free conditions. This catalyst can promote the

Table 2. Recyclability of P_4VPy–CuI.

Run	1	2	3	4	5	6	7	8
Time(min)	22	22	25	25	25	30	35	35
Yield (%)[a]	92	92	92	89	90	90	89	89

yields and reaction times over 8 runs without appreciable loss in its efficiency. Moreover, high yields of products, short reaction times, ease of work-up and clean procedure are the most important advantages of this method which make this procedure useful.

Acknowledgements

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