

# Copper iodide nanoparticles on poly(4-vinylpyridine): A new and efficient catalyst for the synthesis of 1,8-dioxooctahydroxanthenes under solvent-free conditions

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**Abstract.** Poly(4-vinylpyridine)-supported nanoparticles of copper(I) iodide is reported as a new, efficient and recyclable catalyst for the synthesis of 1,8-dioxooctahydroxanthenes under solvent-free conditions. This catalyst can be recovered by simple filtration and recycled up to 10 consecutive runs without losing of its efficiency.

**Keywords.** Poly(4-vinylpyridine) supported; nano particles; copper(I) iodide; 1,8-dioxooctahydroxanthenes; 1,3-dicarbonyl compounds.

## 1. Introduction

Xanthenes and benzoxanthenes are important class of compounds that received significant attention from many pharmaceutical and organic chemists essentially because of the broad spectrum of their biological and pharmaceutical properties such as antibacterial,<sup>1</sup> anti-inflammatory,<sup>2</sup> and antiviral<sup>3</sup> properties. Furthermore, these compounds are used as dyes,<sup>4</sup> fluorescent material for visualization of biomolecules<sup>5</sup> and in laser technologies due to their useful spectroscopic properties.<sup>6</sup> In particular, xanthenediones constitute a structural unit in a number of natural products and have been used as versatile synthase because of the inherent reactivity of the inbuilt pyran ring.<sup>7</sup> Therefore, various synthetic procedures have been developed for the preparation of xanthenediones.<sup>8–16</sup> However, some of these methods involve the use of expensive reagents, toxic solvents, tedious work-up, low yields, long reaction times and harsh reaction conditions. Under this light, there is a scope to develop an alternative method for the synthesis of xanthenes derivatives. Polymer-supported reagents have more and more attracted attention as insoluble material in organic synthesis.<sup>17</sup> They

recommend rewards such as reaction monitoring as well as improved safety, more than ever before when the non-supported reagents are toxic or unsafe as they can be easily removed from reaction medium and recycled.<sup>18</sup> Additionally, employing an excess amount of reagent is permitted without the need for further purification. In recent years, nano-catalysis has emerged as a sustainable and competitive alternative to conventional catalysis 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.<sup>19</sup> In particular, the immobilization of copper(I) salts nanoparticles (CuNPs) on high-surface-area allows a higher stability and dispersity of the particles as well as further exploitation of the special activity and recycling properties of the catalyst.

## 2. Experimental

### 2.1 General

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

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## 2.2 General procedure for preparation of the polymer supported catalyst

CuI (0.381 mg) was dissolved in 30 mL ethanol, and magnetically stirred at reflux temperature for 4 h under a nitrogen atmosphere in the presence of dry poly(4-vinylpyridine) (1.0 g, mesh 50–60). The solvent was drawn off and the resin washed with CH<sub>3</sub>CN (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<sup>-1</sup>. 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<sup>-1</sup> of resin.

## 2.3 Determination of the copper content in P<sub>4</sub>VPy-CuI

The P<sub>4</sub>VPy-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 analysed 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<sup>-1</sup> of prepared catalyst. The same procedure was used to measure the leaching accounts of supported catalyst after 8 consecutive runs.

## 2.4 General procedure

A mixture of dimidone or cyclohexandione (2 mmol), aldehyde (1 mmol) and poly(4-vinylpyridine)-CuI (0.1 g), was heated in an oil bath (80°C) for the appropriate time as shown in table 1. After completion, (monitored by TLC), the mixture was allowed to cool, ethylacetate (10 mL) was added and the catalyst was recovered to use subsequently by filtration. Evaporation of the solvent from the filtrate and recrystallization of the solid residue from hot ethanol affords the pure products in high yields. The spectral and analytical data for new compounds are as follow:

2.4a *Selected spectral data:* Table 1, entry 18: White solid, mp: 270–273°C; IR (KBr)  $\nu_{\max}$ /cm<sup>-1</sup>: 3070, 2950, 2900, 2220, 1652, 1619, 1356, 1200, 1173, 1125, 958, 830, 610, 550; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): d (ppm) 1.95–2.11 (m, 4H), 2.30–2.42 (m, 4H), 2.57–2.73 (m, 4H), 4.84 (s, 1H), 7.44 (d, J 8.0 Hz, 2H), 7.53 (d, J 8.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):

**Table 1.** Synthesis of 1,8-dioxooctahydroxanthenes catalysed by P<sub>4</sub>VPy-CuI.

Entry	Aldehyde	R	Time (min)	Yield (%) <sup>a</sup>	M. P. (°C)	
					Found	Reported
1	PhCHO	CH <sub>3</sub>	13	88	203–204	202–204 <sup>16</sup>
2	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	CH <sub>3</sub>	15	89	261–262	260–262 <sup>16</sup>
3	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	CH <sub>3</sub>	10	89	165–167	165–166 <sup>16</sup>
4	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CHO	CH <sub>3</sub>	7	90	222–224	223–225 <sup>16</sup>
5	2-ClC <sub>6</sub> H <sub>4</sub> CHO	CH <sub>3</sub>	10	90	225–227	226–227 <sup>16</sup>
6	4-ClC <sub>6</sub> H <sub>4</sub> CHO	CH <sub>3</sub>	8	90	225–226	226–228 <sup>16</sup>
7	4-FC <sub>6</sub> H <sub>4</sub> CHO	CH <sub>3</sub>	10	88	227–228	226–227 <sup>16</sup>
8	4-MeC <sub>6</sub> H <sub>4</sub> CHO	CH <sub>3</sub>	12	87	217–218	215–216 <sup>16</sup>
9	2-MeOC <sub>6</sub> H <sub>4</sub> CHO	CH <sub>3</sub>	25	87	189–191	188–190 <sup>16</sup>
10	4-MeOC <sub>6</sub> H <sub>4</sub> CHO	CH <sub>3</sub>	28	85	241–243	242–243 <sup>16</sup>
11	3,4-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHO	CH <sub>3</sub>	36	86	176–178	175–176 <sup>16</sup>
12	4-CNC <sub>6</sub> H <sub>4</sub> CHO	CH <sub>3</sub>	14	85	215–217	217–218 <sup>16</sup>
13	4-OHC <sub>6</sub> H <sub>4</sub> CHO	CH <sub>3</sub>	35	86	248–250	247–248 <sup>16</sup>
14	PhCHO	H	12	90	266–268	267–269 <sup>21</sup>
15	4-BrC <sub>6</sub> H <sub>4</sub> CHO	H	9	90	283–285	284–286 <sup>21</sup>
16	4-ClC <sub>6</sub> H <sub>4</sub> CHO	H	8	91	284–286	286–288 <sup>21</sup>
17	4-MeOC <sub>6</sub> H <sub>4</sub> CHO	H	30	86	202–203	200–201 <sup>21</sup>
18	4-CNC <sub>6</sub> H <sub>4</sub> CHO	H	12	90	273–275	–
19	3-BrC <sub>6</sub> H <sub>4</sub> CHO	H	8	87	281–283	–
20	3-MeOC <sub>6</sub> H <sub>4</sub> CHO	H	30	88	192–194	–

<sup>a</sup>Isolated yield

d (ppm) 20.2, 27.1, 32.3, 36.8, 110.2, 115.8, 119.10, 129.4, 132.0, 149.7, 164.5, 196.5.

Table 1, entry 19: White solid, mp: 281–283°C; IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3070, 2910, 2890, 1660, 1620, 1560, 1470, 1420, 1358, 1200, 1170, 1122, 957, 800, 680; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): d (ppm) 1.95–2.1 (m, 4H), 2.30–2.44 (m, 4H), 2.55–2.63 (m, 2H), 2.66–2.73 (m, 2H), 4.79 (s, 1H), 7.11 (t, J 7.6 Hz, 1H), 7.26–7.36 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): d (ppm) 20.3, 27.2, 31.6, 36.9, 116.3, 122.3, 127.7, 129.6, 131.0, 146.6, 164.3, 196.4.

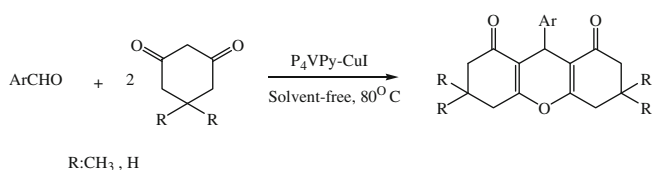
Table 1, entry 20: White solid, mp: 192–194°C; IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 3070, 2950, 1650, 1605, 1580, 1450, 1360, 1265, 1220, 1200, 1180, 1130, 1050, 960; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): d (ppm) 1.99–2.1 (m, 4H), 2.3–2.45 (m, 4H), 2.54–2.71 (m, 4H), 3.81 (s, 3H), 4.83 (s, 1H), 6.69–6.71 (dd, J<sub>1</sub> 8.0 Hz, J<sub>2</sub> 1.6 Hz, 1H), 6.89–6.95 (m, 2H), 7.17 (t, J 8.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): d (ppm) 20.3, 27.2, 31.5, 37.0, 55.2, 111.5, 114.5, 116.8, 121.0, 129.0, 146.0, 159.4, 164.0, 196.5.

### 3. Results and discussion

We report here the applicability of a new, green and reusable catalytic system based on Cu(I) nanoparticles supported by poly(4-vinylpyridine) (P<sub>4</sub>VPy-CuI) for one-pot multicomponent synthesis of 1,8-dioxooctahydroxanthenes from cyclic 1,3-dicarbonyl compounds (dimedone and 1,3-cyclohexadione) with aldehydes in the absence of solvent (scheme 1).

The copper(I) iodide 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 N<sub>2</sub> atmosphere in EtOH to afford the polymer-supported CuI nanoparticles. This method was developed for the effective synthesis of copper nanoparticles incorporated heterogeneously as catalyst in some organic reactions.<sup>20</sup>

Scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, atomic absorption and IR experimental techniques were used to characterize the catalyst. The SEM image of the prepared catalyst indicated

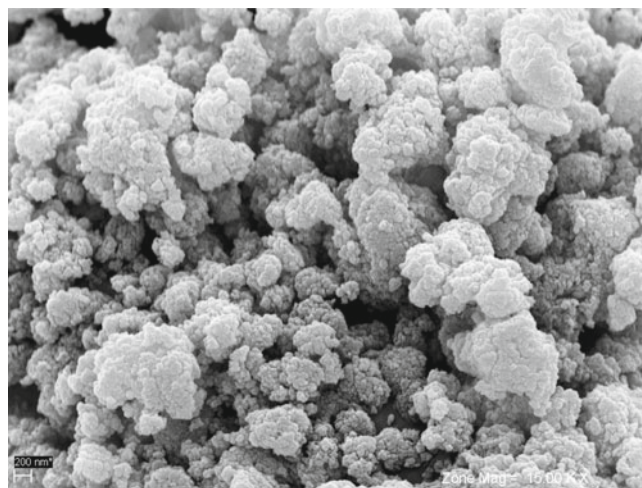


**Scheme 1.** Synthesis of 1,8-dioxooctahydroxanthene derivatives under solvent-free conditions.

that CuI nanoparticles were homogeneously immobilized on poly(4-vinylpyridine) surface (figure 1).

According to the SEM images of P<sub>4</sub>VPy-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<sub>4</sub>VPy-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 broadening using the Debye–Scherrer formula (obtained size: 75 nm). At first, for the optimization of the reaction conditions, the reaction between benzaldehyde and dimidone was investigated as a model and its behaviour was studied under a variety of conditions. The best result was achieved by carrying out the reaction of benzaldehyde and dimidone (with 1:2 mol ratio) in the presence of 0.1 g of P<sub>4</sub>VPy-CuI in the absence of solvent (table 1, entry 1). Using these optimized conditions, the reaction of various aromatic aldehydes, containing electron-donating and electron-withdrawing groups, was explored. All the products were cleanly 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 relatively short reaction times.

It is also noteworthy that resin does not suffer from extensive mechanical degradation after running. For a true heterogeneous catalyst, supported catalyst should not leach to the reaction mixture. Moreover, the recyclability of the supported catalyst is also important. To investigate these properties for our introduced catalyst, the reaction of benzaldehyde with dimidone was selected again as model (table 2). After completion of the reaction, the recovered catalyst was washed with acetone and after dryness was reused in the next similar



**Figure 1.** SEM image of poly(4-vinylpyridine)-supported CuI nanoparticles.

**Table 2.** Recyclability study of P<sub>4</sub>VPy–CuI.

Run	1	2	3	4	5	6	7	8
Tim (min)	12	12	15	16	18	20	20	25
Yield (%) <sup>a</sup>	89	89	87	86	84	84	81	79

<sup>a</sup>Isolated yield

run. This procedure was repeated for 8 consecutive runs and the results of this study are represented in table 2.

The results showed that the polymer supported CuI can be re-used up to 8 runs without any significant decrease in the yields. Almost consistent activity was observed over 8 runs. However, it can be seen that as the recycling steps were increased, slight decrease in the rate of the reactions was observed. Next, we checked the leaching of CuI into the reaction mixture from the poly(4-vinyl pyridine) support using ICP-AES. The difference between the copper content of the fresh and re-used catalyst (8th run) was only 3% which indicated the low leaching amount of copper iodide catalyst into the reaction mixture.

#### 4. Conclusion

We have developed a mild, simple and green procedure for the one-pot synthesis of 1,8-dioxooctahydroxanthenes using recyclable P<sub>4</sub>VPy–CuI under solvent-free conditions. The introduced catalyst can promote the yields and reaction times. This catalyst showed excellent activity during 8 consecutive runs with very low leaching amounts of supported catalyst into the reaction mixture. Moreover, ease of work-up and clean procedure, will make the present method an useful and important addition to the present methodologies for the synthesis of 1,8-dioxooctahydroxanthenes.

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