



Short communication

Bi (NO₃)₃·5H₂O and cellulose mediated Cu-NPs – A highly efficient and novel catalytic system for aerobic oxidation of alcohols to carbonyls and synthesis of DFF from HMF



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ARTICLE INFO

Article history:

Received 5 October 2015

Received in revised form 23 December 2015

Accepted 4 January 2016

Available online 7 January 2016

Keywords:

Cellulose

Cu-nanoparticles

Bismuth nitrate

Oxidation

Alcohols

HMF

Sustainable

ABSTRACT

A highly efficient and versatile catalytic system for oxidation of primary and secondary aromatic alcohols to carbonyls has been developed. High efficiency, general synthetic applicability, broader functional group tolerance and versatility towards oxidation of both primary and secondary aromatic alcohols are the key features of this green and sustainable protocol. Selective oxidation of 5-hydroxymethyl furfural (HMF) to biofuel 2,5-diformylfuran (DFF) has been observed in excellent yields. Use of sustainable bio-polymer cellulose as a Cu-nanoparticle support makes the catalytic system environmentally benign.

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1. Introduction

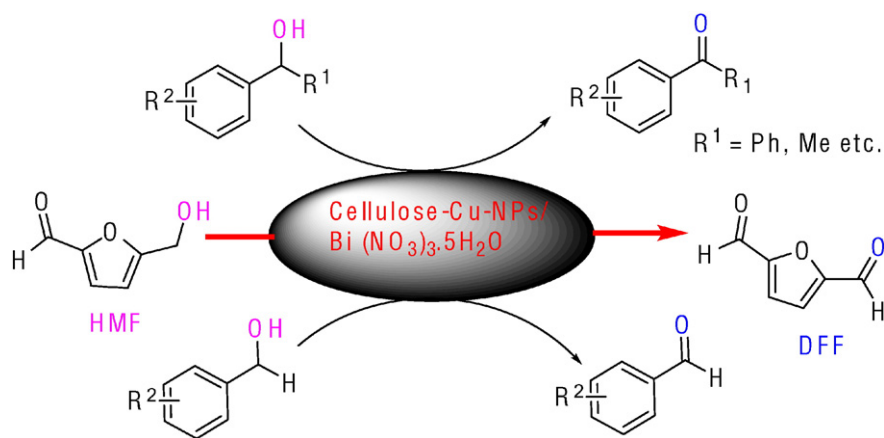
Oxidation of alcohol to carbonyl is one of the most widely studied reactions in synthetic chemistry due to the versatile applicability of these products as important precursors and intermediates for large number of drugs, vitamins, fragrances and biofuels [1,2]. In recent years, the production of value added products and platform chemicals from oxidation of renewable chemical building block 5-hydroxymethyl furfural (HMF) gets tremendous importance both from academia and industry point of view [3]. Selective oxidation of HMF generates symmetrical 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HMFA), 2,5-furandicarboxylic acid (FDCA) and 2-formyl furan carboxylic acid (FFCA) which are promising building block of fuels, polymers, drugs etc. Especially DFF have numerous applications in the synthesis of polymers, pharmaceuticals, antifungal agents, precursor of macrocyclic ligands and various functional materials [4]. Although there are numbers of efficient methodology have been documented so far on selective oxidation of HMF to DFF but development of a simple, sustainable, economical and efficient protocol in this instance is highly recommendable [4–10]. Plethora of oxidizing agents is available for

oxidation of alcohols in which most of them are often toxic, release considerable amounts of by-products, have very poor atom economy, required in stoichiometric amounts and more importantly the purification processes are demanding and laborious [11]. Use of heterogeneous catalyst with respect to homogeneous one minimizes the risk of by product generation, catalyst-product separation and purification of the desired product. Recently, much attention has been received on development of metal-catalysed aerobic alcohol oxidation strategies because of economical and environmental concern [1,11]. In this endeavour, development of the environment friendly, sustainable, cost effective and highly efficient heterogeneous catalytic system for alcohol oxidation is utmost essential. In continuation of our earlier works on alcohol oxidation [12–14] and cellulose supported metal nanoparticles (NPs) [14–18], we report here a novel catalytic system Bi (NO₃)₃·5H₂O and cellulose mediated Cu-NPs for oxidation of primary/secondary aromatic alcohols to carbonyls and HMF to DFF under atmospheric oxygen in acetonitrile solvent (Scheme 1).

Catalytic oxidations using molecular oxygen are particularly attractive both from economic and environmental point of view [19]. This highly efficient catalytic system consists of bismuth nitrate pentahydrate, Bi (NO₃)₃·5H₂O and cellulose supported Cu-NPs. Bi (NO₃)₃·5H₂O is relatively non-toxic, non-carcinogenic, readily available and cheap [20]. Sustainable bio-polymer cellulose as a metal NP support resulted well defined crystalline Cu-NPs with excellent catalytic activity

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Scheme 1. Oxidation of primary and secondary aromatic alcohol to carbonyls using Bi(NO₃)₃·5H₂O and cellulose mediated Cu-NPs.

and thermal stability [21,22]. Combination of these two oxidizing agents provides this novel and effective catalytic system for oxidation of primary and secondary aromatic alcohols to carbonyls in very short reaction time with high product yields. Recently, nitroxide catalysed aerobic alcohol oxidation reactions get lots of importance [23]. Only a very few reports have been developed so far using Bi(NO₃)₃·5H₂O as a successful oxidizing agent [24–27]. From the extensive literature survey it comes to our knowledge that this is the first catalytic system where Bi(NO₃)₃·5H₂O and cellulose mediated Cu-NPs are used for successful oxidation of both the primary and secondary aromatic alcohols to carbonyls and especially HMF to DFF (85% conversion) under oxygen atmosphere. Earlier reported methods using Bi(NO₃)₃·5H₂O can either oxidize primary aromatic alcohols to aldehydes [25,26] or secondary alcohols to ketones [24]. This new protocol was found to be extremely efficient towards the oxidation of secondary aromatic alcohol to ketones with 100% conversion.

2. Results and discussions

An initial experiment on oxidation of secondary aromatic alcohol was carried out using diphenyl methanol **1a** as a model substrate with 1.0 mmol Bi(NO₃)₃·5H₂O in acetonitrile solvent under oxygenated atmosphere at 80 °C. This initial experiment resulted in 30% conversion of **1a** to diphenyl methanone **2a** (entry 1, Table 1). Increasing the reaction time (entries 2&3, Table 1) under the same condition provided slightly higher conversion rate (40%). Loading of 2.0 mmol Bi(NO₃)₃·5H₂O also did not show any satisfactory conversion (entry 4, Table 1). More interestingly, the employment of 20 mol% (0.056 g) cellulose mediated Cu-NPs with 1.0 mmol Bi(NO₃)₃·5H₂O gave 80% conversion of **1a** to **2a** in 10 min (entry 6, Table 1). Subsequently, enhancement of reaction time to 20 min led to 90% conversion (entry 7, Table 1) and finally 100% conversion was observed in 30 min using the combined catalytic system under the oxygenated atmosphere at 80 °C in acetonitrile solvent (entry 8, Table 1). Switching the reaction temperature to 60 °C also showed the 100% conversion (entry 9, Table 1). Catalyst loading studies (entries 9, 10, 11 & 12, Table 1) confirmed that 0.75 mmol Bi(NO₃)₃·5H₂O and 20 mol% cellulose mediated Cu-NPs are sufficient for 100% conversion of **1a** to **2a**. Performing the reaction with different metal nitrates/nitrites (entry 13, Table 1) and water as a solvent (entry 14, Table 1) resulted 0% conversion. 39% conversion was obtained in DMF solvent under the condition described in entry 15, Table 1. It is interesting to observe that only cellulose supported Cu-NPs as a catalyst did not show any conversion (0%) of **1a** to **2a** at all (entry 5, Table 1). Thus, we obtained the optimized reaction condition (entry 10, Table 1): diphenyl methanol **1a** (1.0 mmol), Bi

Table 1
Optimization studies on oxidation of diphenyl methanol **1a** to diphenyl methanone **2a**.

Entry	Bi(NO ₃) ₃ ·5H ₂ O	Cellulose-Cu-NPs	Solvent	Temperature	Time	Conv. (%) ^b
1	1.0 mmol	–	MeCN	80 °C	30 min	30
2	1.0 mmol	–	MeCN	80 °C	3 h	40
3	1.0 mmol	–	MeCN	80 °C	10 h	40
4	2.0 mmol	–	MeCN	80 °C	10 h	40
5	–	20 mol%	MeCN	80 °C	10 h	0
6	1.0 mmol	20 mol%	MeCN	80 °C	10 min	80
7	1.0 mmol	20 mol%	MeCN	80 °C	20 min	90
8	1.0 mmol	20 mol%	MeCN	80 °C	30 min	100
9	1.0 mmol	20 mol%	MeCN	60 °C	30 min	100
10	0.75 mmol	20 mol%	MeCN	60 °C	30 min	100
11	0.5 mmol	20 mol%	MeCN	60 °C	30 min	80
12	1.0 mmol	10 mol%	MeCN	60 °C	30 min	85
13	1.0 mmol ^c	10 mol%	MeCN	60 °C	30 min	0
14	1.0 mmol	10 mol%	H ₂ O	100 °C	3 h	0
15	1.0 mmol	10 mol%	DMF	60 °C	3 h	39

^aReaction condition: diphenyl methanol **1a** (1.0 mmol), Bi(NO₃)₃·5H₂O (0.75 mmol), cellulose-Cu-NPs (20 mol%), MeCN (10 mL), 30 min, 60 °C, air. ^bDetermined by GC–MS. ^cNaNO₂, NaNO₃, KNO₃.

The bold data indicates the optimized condition for oxidation of secondary alcohol to ketone.

Table 2
Oxidation of secondary alcohols to ketones^a by Bi(NO₃)₃·5H₂O and cellulose mediated Cu-NPs.

Entry	R ¹	R ²	Conv. (%) ^b	Yield (%) ^c
1	Ph	Ph	100	99
2	2-NH ₂ Ph	Ph	99	98
3	2-OH,4-OMePh	Ph	99	97
4	Ph	Me	99	97
5	4-BrPh	Me	99	95
6	2-OHPh	Me	99	96
7	4-OHPh	Me	99	96
8	Vinyl benzene	Ph	>99	97

^a Reaction condition: substrate (1.0 mmol), Bi(NO₃)₃·5H₂O (0.75 mmol), cellulose-Cu-NPs (20 mol%), MeCN (10 mL), 30 min, 60 °C, air.

^b Determined by GC–MS.

^c Isolated yield.

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