Short communication

Bi (NO$_3$)$_3$·5H$_2$O 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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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 (HMFCA), 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 (NO$_3$)$_3$·5H$_2$O 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 (NO$_3$)$_3$·5H$_2$O and cellulose supported Cu-NPs. Bi (NO$_3$)$_3$·5H$_2$O 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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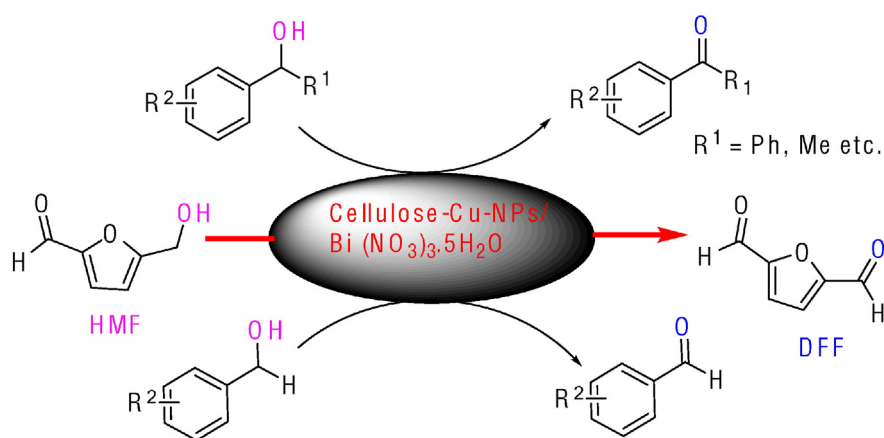
Scheme 1. Oxidation of primary and secondary aromatic alcohol to carbonyls using Bi $(NO_3)_3 \cdot 5H_2O$ and cellulose mediated Cu-NPs.

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 $(NO_3)_3 \cdot 5H_2O$ 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 $(NO_3)_3 \cdot 5H_2O$ 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 $(NO_3)_3 \cdot 5H_2O$ 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 $(NO_3)_3 \cdot 5H_2O$ 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 $(NO_3)_3 \cdot 5H_2O$ 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 $(NO_3)_3 \cdot 5H_2O$ 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 $(NO_3)_3 \cdot 5H_2O$ 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 $(NO_3)_3 \cdot 5H_2O$	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%	H₂O	100 °C	3 h	0
15	1.0 mmol	10 mol%	DMF	60 °C	3 h	39

[a]Reaction condition: diphenyl methanol **1a** (1.0 mmol), Bi $(NO_3)_3 \cdot 5H_2O$ (0.75 mmol), cellulose-Cu-NPs (20 mol%), MeCN (10 mL), 30 min, 60 °C, air. [b]Determined by GC–MS.
[c]NaNO₂, 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 $(NO_3)_3 \cdot 5H_2O$ and cellulose mediated Cu-NPs.

Entry	R^1	R^2	Conv. (%)[b]	Yield (%)[c]
1	Ph	Ph	100	99
2	2-NH₂Ph	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 $(NO_3)_3 \cdot 5H_2O$ (0.75 mmol), cellulose-Cu-NPs (20 mol%), MeCN (10 mL), 30 min, 60 °C, air.
[b] Determined by GC–MS.
[c] Isolated yield.
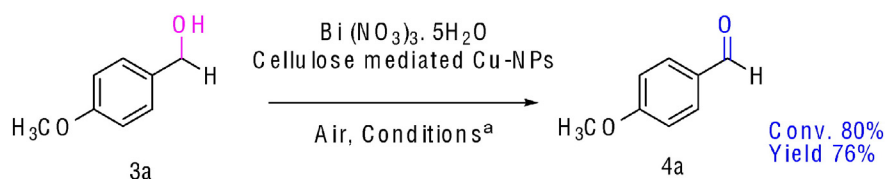
Scheme 2. Oxidation of 4-Methoxy benzyl alcohol **3a** to 4-Methoxy benzaldehyde **4a**. [a]Reaction condition: 4-Methoxy benzyl alcohol **3a** (1.0 mmol), Bi (NO$_3$)$_3$·5H$_2$O (0.75 mmol), cellulose-Cu-NPs (20 mol%), MeCN (10 mL), 60 min, 80 °C, air. [b]Determined by GC–MS. [c]Isolated yield.

(NO$_3$)$_3$·5H$_2$O (0.75 mmol), cellulose-Cu-NPs (20 mol%), MeCN (10 mL), 30 min, 60 °C and oxygenated atmosphere. Solubility of Bi (NO$_3$)$_3$·5H$_2$O was found to be varied in different solvents used. It dissolves in acetonitrile and water sparingly with giving a white cloudy solution in the reaction mixture. Bi (NO$_3$)$_3$·5H$_2$O dissolves completely in DMF with a clear solution. Preparation method and characterization data (XRD, TEM etc.) of cellulose mediated Cu-NPs [14–17] are discussed in supporting information section.

Having the optimized reaction conditions in hand (entry 10, Table 1), we next tested the oxidation of a series of substituted secondary aromatic alcohols. As shown in Table 2, all the secondary aromatic alcohols (entries 1–8, Table 2) were found to be successfully converted to their respective carbonyls with almost 100% selectivity with excellent yield (95–99%). Very negligible substituent effect has been observed in the oxidation process using this efficient catalytic system.

To further probe the potentiality of this new catalytic system, we investigated the oxidation of primary aromatic alcohols under open air atmosphere. We began to examine the proposed study by taking 4-Methoxy benzyl alcohol **3a** as a model substrate (Scheme 2). Preliminary results clearly suggested the feasibility of the proposed scheme. From the optimization study on oxidation of **3a** to **4a** we finally got the most exclusive condition for highest conversion (80%) with high yield percentage (76%) of the desired product **4a**. The optimized reaction condition was: 4-Methoxy benzyl alcohol **3a** (1.0 mmol), Bi (NO$_3$)$_3$·5H$_2$O (0.75 mmol), cellulose-Cu-NPs (20 mol%), MeCN (10 mL), 60 min, 80 °C and oxygenated atmosphere.

Utilizing the optimized reaction conditions, the scope and limitations in oxidation of primary aromatic alcohols were studied and the results are shown in Table 3. A variety of benzylic alcohols (entries 1–8, Table 3), heteroaryl alcohols (entries 9&10, Table 3) and cinnamyl alcohols (entries 11–14, Table 3) were efficiently oxidizes to the corresponding aldehydes in moderate to high yield using the catalytic

system under ambient conditions. Benzylic alcohols having electron withdrawing group (entries 5–8, Table 3) afforded slightly less product yield as compared to electron donating counterparts (entries 1–4, Table 3). It is noteworthy to mention that more reaction time is required to obtain high yield of heteroaryl and cinnamyl aldehydes. Oxidation of heteroaryl and cinnamyl alcohols using this sustainable catalyst afforded moderate yield (55–68%) of desired aldehydes. Our catalyst was found to be totally inert towards the oxidation of long chain aliphatic alcohols. No over oxidized products were observed during the oxidation of primary and secondary aromatic alcohols. All the other functional groups (e.g., –OMe, –OH, –NO$_2$, –Cl, –Br, –N (CH$_3$)$_2$, and –NH$_2$) were well tolerated in oxidation process using this versatile catalytic system.

Next we studied the oxidation of 5-hydroxymethyl furfural (HMF) using the proposed catalytic system. HMF with two different active functional groups has four different oxidation pathways (**path a–d**) which can afford four different value added products as shown in Scheme 3. It was found that our catalytic system selectively oxidizes the hydroxymethyl group of HMF to formyl group with affording diformylfuran (DFF) as a final product (**path a**). No over oxidized products like FFCA, FDCA, HMFCA were observed during the oxidation process. The proposed catalytic system was found to be totally inert towards the oxidation of formyl group of HMF. The optimized reaction condition for oxidation of HMF to DFF was: HMF (1.0 mmol), Bi (NO$_3$)$_3$·5H$_2$O (0.75 mmol), cellulose-Cu-NPs (20 mol%), MeCN (10 mL), 80 °C, 120 min, air. Isolated yield of DFF is 82% (85% conversion).

Studies on the reusability of the catalytic system for the oxidation of different alcohols confirmed the non-reusability/non-recyclability of the catalytic system. This may be due to the generation of Cu (II) in the reaction cycle. Appeared blue colour solution in the reaction vessel indicates the generation of Cu (II). From the literature survey [19,28], it can be summarized that Bi (NO$_3$)$_3$·5H$_2$O is responsible for the oxidation of Cu (0)/Cu (I) to Cu (II) with concomitant conversion of NO$_3$ to NO$_2$. The irreversible conversion of Cu (0)/Cu (I) to Cu (II) during the reaction process can be regarded as the main cause for the non-reusability/non-recyclability. Only recollected cellulose (after work-up) can be used further for synthesis of Cu-NPs. Further studies on intrinsic catalytic role and synthetic application of the reactions using this catalytic system is under investigation.

Table 3
Oxidation of primary aromatic alcohols to aldehydes[a] by Bi (NO$_3$)$_3$·5H$_2$O and cellulose mediated Cu-NPs.

| Entry	R	Time	Conv. (%)[b]	Yield (%)[c]
1	4-OMePh	60 min	80	76
2	3,4-OMePh	60 min	80	74
3	4-N(CH$_3$)$_2$Ph	60 min	80	73
4	2-OHPh	60 min	75	69
5	4-ClPh	60 min	75	68
6	2,4-ClPh	60 min	75	66
7	4-NO$_2$Ph	60 min	70	65
8	2-NO$_2$Ph	60 min	70	65
9	3-Pyridyl	120 min	60	55
10	2-Indolyl	120 min	60	56
11	Cinnamyl	120 min	70	65
12	4-OMe Cinnamyl	120 min	75	68
13	4-N(CH$_3$)$_2$ Cinnamyl	120 min	75	67
14	4-NO$_2$ Cinnamyl	120 min	70	62

[a] Reaction condition: substrate (1.0 mmol), Bi (NO$_3$)$_3$·5H$_2$O (0.75 mmol), cellulose-Cu-NPs (20 mol%), MeCN (10 mL), 80 °C, air.
[b] Determined by GC–MS.
[c] Isolated yield.

3. Conclusion

From the overall discussion it can be concluded that our new catalytic system was found to be very effective towards the oxidation of secondary aromatic alcohols to ketones with almost 100% convertibility. 60–80% conversion rate was found in the oxidation of primary aromatic alcohols to aldehydes under this milder reaction condition. Oxidation of 5-hydroxymethyl furfural to 2,5-diformylfuran (82% yield) was one of the great achievements by this sustainable catalytic system. Finally we developed an economical, environmentally benign, highly efficient and versatile catalytic system cellulose mediated Cu-NPs with bismuth nitrate pentahydrate for oxidation of aromatic alcohols as well as HMF to DFF. This new methodology can be applicable in industrial synthesis of DFF and other carbonyls from aromatic alcohols with the emphasis on economic and environmental issues.
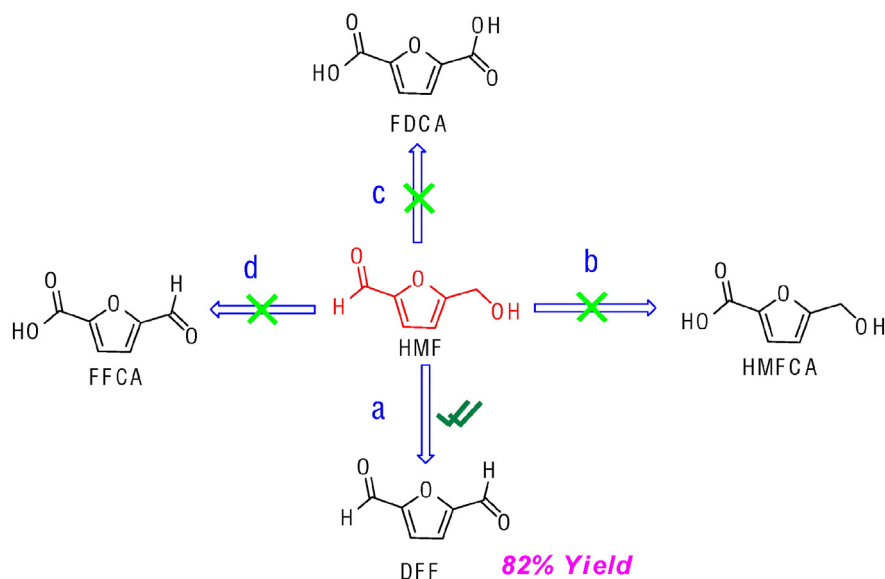
Scheme 3. Possible way of oxidation of HMF to different value added products.

Acknowledgements

Appendix A. Supplementary data

Experimental details and characterization data of Cu-NPs on cellulose template, and copies of the NMR spectra of all the products. This material is available free of charge via the Internet at http://d.dor.org/10.1016/j.catcom.2016.01.003.

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