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Highly Efficient Aerobic Oxidation of Biomass-derived 5-Hydroxymethyl Furfural to Produce 2, 5-Diformylfuran in the Presence of Copper Salts

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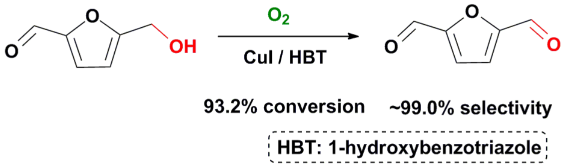

Based on the catalysis of copper salt, an efficient and selective oxidation of 5-hydroxymethyl furfural to 2, 5-diformylfuran with molecular oxygen as the oxidant has been developed.

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PAPER

Highly Efficient Aerobic Oxidation of Biomass-derived 5-Hydroxymethyl Furfural to Produce 2, 5-Diformylfuran in the Presence of Copper Salts

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An efficient and selective oxidation of 5-hydroxymethylfurfural (HMF) to produce 2, 5-diformyl furan (DFF) has been achieved using a cheap copper (I) iodate as catalyst in dimethylsulfoxide solvent. The effect of different mediators including *N*-hydroxyphthalimide, 2, 2, 6, 6-tetramethyl piperidine-1-oxyl radical, 1-hydroxybenzotriazole (HBT) and *N*-methylmorphilone *N*-oxide were investigated. It was found that the combination of CuI-HBT favors the generation of DFF in the oxidation. Moreover, the molecular oxygen as the oxidant is superior to *tert*-butyl hydroperoxide and hydrogen peroxide as oxidant in this catalytic process. For instance, a 93.2% conversion and 99% selectivity for DFF was obtained under 0.3 MPa of O_2 at 130 ºC for 10 h. The effects of catalyst amount, temperature and solvent were also discussed. Furthermore, a hypothetical reaction mechanism is proposed.

1. Introduction

The selective oxidation of alcohols into aldehydes is one of the most important transformations in both laboratory and industrial synthetic chemistry.[1-4] In the transformation of biomass feedstock, the oxidation of hydroxy to carbonyl group is also significant to the conversion of bio-based platform compounds. For example, the selective and partial oxidation of 5-hydroxymethyl furfural (HMF) leads to the formation of 2, 5-diformylfuran (DFF), which has potential applications in the synthesis of drugs[5], fungicides, and new functional polymers.[6, 7] Up to now, high yields of DFF could be attained under non-catalytic condition through the use of stoichiometric oxidants[8] or the assistance of electrophilic agents.[9] However, from the viewpoints of economy and sustainability, the catalytic routes for DFF production are more valuable in the practical application. In the early work, hydrogen peroxide (H_2O_2) was employed as the oxidant with the titanium silicalite as a catalyst.[10] However, the maximum yield for DFF is only 25% during catalytic process. Moreover, chloroperoxidase-catalyzed oxidation of HMF with H_2O_2 as the oxidant was studied in which a 60-74% selectivity for DFF was obtained.[11] Besides, Amarasekara et al.[12] reported that HMF could be oxidized to DFF by sodium hypochlorite (NaOCl) with Mn(III)-salen catalyst and 63-89% yield was attained in a phosphate buffer-CH_2Cl_2 solution.

In recent years, the use of oxygen or air as oxidant was extensively investigated. Verdeguer et al. found that a 19% yield of DFF was obtained under a high temperature and neutral pH when a Pt/C catalyst was used in the aerobic oxidation of HMF.[13] In addition, Moreau and coworkers[14,15] reported that the oxidation of HMF with oxygen using the V_2O_5/TiO_2 catalyst, in which a 90% yield of DFF was achieved at 90 ºC under 1.6 MPa for 4 h. Futhermore, Navarro et al.[16] reported a 50% conversion and 98% selectivity of DFF was obtained for the aerobic oxidation of HMF in the presence of vanadyl complexes supported SBA-15 catalyst. Sádaba et al.[17] detected the catalytic performance of zeolite-supported vanadia catalysts for the aerobic oxidation of HMF to DFF in organic solvent. Under optimized conditions, a reaction selectivity towards DFF of >99% at 84% HMF conversion was obtained using 1 wt% V_2O_5/H-beta as the catalyst. Otherwise, Nie et al.[18] reported that activated carbon-supported Ru clusters (Ru/C) efficiently catalyzed HMF oxidation to DFF with a high yield of about 96% at 383 K and 2.0 MPa O_2 in toluene solvent. Very recently, the same group also investigated the aerobic oxidation of HMF to DFF with the manganese oxide octahedral molecular sieve (OMS-2) and a high yield of 97.2% at 383 K and 0.5 MPa O_2 in *N, N*-dimethyl formamide (DMF) solvent. [19] Also, the Ag-OMS-2 catalyst was found to exhibit high catalytic activity and product selectivity where a 99% yield of DFF was achieved with oxygen molecule as the oxidant under sutiable conditions.[20] The above numerous heterogeneous catalyst showed good catalytic performance for the production of DFF from HMF; however, the preparation of the catalyst is complicate and disadvantageous in industrial application. In the homogeneous catalytic process, the oxidation of HMF with molecular oxygen using a mixed Co/Mn/Zr/Br system has been carried out in which 57% yield of DFF was attained.[21] Besides, Ma et al.[22] investigated that the aerobic oxidation of HMF with the $Cu(NO_3)_2/VOSO_4$ catalytic system and a 98% yield of DFF was obtained in acetonitrile solvent. However, all these systems need the function of expensive metal (such as Pt, V and Ru, etc.) or corrosive component (e.g. bromide). So, developing more cost-efficient and environmentally friendly catalytic system for the oxidation of HMF remains an issue of scientific interest at present.

In this paper, we report a novel homogeneous catalytic method for oxidation of HMF in the presence of copper iodate. It was found that a 92.3% yield of DFF was obtained in dimethyl sulfoxide (DMSO) solvent. The effects of various copper salts, mediators, oxidants and solvents on the activity and DFF selectivity were examined. Along with a wide range of chemical structure and redox properties, the mediators include 1-hydroxybenzotriazole (HBT), N-hydroxyphthalimide (NHPI), 2,2,6,6-tetramethyl piperidine-1-oxyl (TEMPO), *N*-methyl morphilone *N*-oxide (NMO) and 2,4-dichloro-5,6-dicyano benzoquinone (DDQ), etc.. The solvents are tested among DMSO, 1-methylpyrrolidin-2-one (NMP), n-Butanol, toluene, acetonitrile (CH_3CN), γ-Butyrolactone, tetrahydrofuran (THF), *N, N*-dimethyl acetamide (DMAc) and DMF, with different polarity and protic nature. In addition, a possible reaction mechanism was provided based on the obtained data and corresponding experimental phenomena.

2. Experimental Section

2.1 Reagents

Copper (I) iodate, copper (I) chloride, copper (II) dichloride, HMF, $NaNO_2$, HBT, copper (I) bromide, copper (II) bromide, NHPI, TEMPO, NMO, DDQ, *tert*-butyl hydroperoxide (t-BuOOH), and hydrogen peroxide (H_2O_2) are of analytical grade and obtained from commerial source. The DFF as the standard sample is purchased from Alfa Aesar, A Johnson Matthey Company. Oxygen supplied in a high-pressure cylinder is used through a reducing valve without further treatment. DMSO and other solvents are purified by distillation.

2.2 General Procedure for Oxidation of 5-Hydroxymethylfurfural

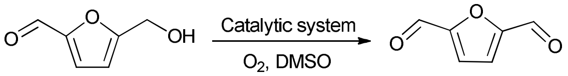
All oxidation experiments are performed in a 120 mL autoclave equipped with the magnetic stirring and automatic temperature control. A typical procedure for the oxidation of HMF is as follows: a DMSO (15 mL) solution of HMF (1.26 g, 0.01 mol), CuI (20.0 mol%) and HBT (7.5 mol%) is charged into the reactor, and the atmosphere inside is replaced with the pure oxygen after the reactor is sealed. Under stirring, oxygen is charged to 0.3 MPa at room temperature and the autoclave is preheated to 130 ºC, and then kept for 10 h. After reaction, the autoclave was cooled and the obtained mixture is analyzed by GC and GC-MS after the excess gas is purged.

2.3 Analysis and Separation of Oxidized Products

The products are analyzed with the internal standard technique by gas chromatography using a flame ionization detector (all products are determined on GC-MC). Moreover, for oxidation of HMF, the product is separated from the product solutions as follows: the reaction mixture is first distilled to remove the solvent DMSO, and then is transferred into a flask and a saturated aqueous $NaHSO_3$ solution is added. The obtained liquid mixtures were stirred for 2 h under N_2 atmosphere and left in a refrigerator for 3 h, and then the resulting solid was collected by filtration. The solid mixtures are washed with an aqueous solution of sodium chloride to remove HMF and by-products. In the following, the washed solid was transferred into a two-neck flask and the HCl solution is added under N_2 atmosphere. The reaction is performed with stirring for 1 h at room temperature and for 2 h at 50 ºC. The product is regenerated and extracted with diethyl ether. After being dried, the diethyl ether layer was distilled to obtain pure DFF as a solid product. As a result, the purity is more than 99% from GC analysis. The difference between the GC yield and separated yield is less than 10%.

3. Result and Discussions

Initially, the oxidation of HMF, as shown in Scheme 1, is performed in DMSO solvent under 0.3 Mpa of O_2 using different copper salts as catalysts. The obtained data are summarized in Table 1. It is found that the conversion of HMF is 20.7% or 21.8% in the presence of single CuCl or $CuCl_2$ at 130 ºC for 10 h, respectively (entries 1 and 2). The conversion is elevated to 24.0% and 25.1 when CuBr and $CuBr_2$ are added as catalysts, respectively (entries 3 and 4). While, the conversion of HMF and the selectivity of DFF respectively adds up to 37.2% and 94.5% when 20 mol% CuI is used as the catalyst (entry 5). In the following, the HBT was employed as the promoter to improve the oxidation. To our surprise, a 93.2% conversion and 99.0% selectivity for DFF is obtained when 7.5 mol% HBT was added as the mediator (entry 6). Furthermore, the combination of CuCl-HBT, $CuCl_2$-HBT, CuBr-HBT and $CuBr_2$-HBT were also investigated, and it was found that a 90.9%, 78.0%, 88.2% and 74.1% conversions of HMF are obtained for 10 h (entries 7, 8, 9 and 10). These data showed that the HBT has prominent mediation for Cu-catalyzed selective oxidation of HMF to DFF with moleculat oxygen. Furthermore, the control experiment was carried out in the presence of single HBT in which only a 26.7% conversion is obtained under similar conditions (entry 11). On the other hand, the oxidation of HMF with t-BuOOH or H_2O_2 as the oxidant was investigated, and the yield of DFF was respectively 68% or 45% in DMSO solvent (entries 12 and 13). This exhibited that the molecular oxygen is more suitable oxidant than t-BuOOH and H_2O_2 for the oxidation of HMF using the combination of CuI and HBT as the catalytic system.



Scheme 1. Oxidation of HMF to DFF with different catalytic systems.

Table 1. Oxidation of HMF to DFF with different catalysts[a]

Entry	Catalyst (mol%)	Conversion (%)[b]	Selectivity (%) [b]
1	CuCl	20.7	99.0
2	$CuCl_2$	21.8	99.0
3	CuBr	24.0	100
4	$CuBr_2$	25.1	99.0
5	CuI	37.2	100
6	CuI+HBT	93.2	99.0
7	CuCl+HBT	90.9	98.0
8	$CuCl_2$+HBT	78.0	98.0
9	CuBr+HBT	88.2	99.0
10	$CuBr_2$+HBT	74.1	98.0
11	HBT	26.7	90.0
12[c]	CuI+HBT	69.2	98.0
13[d]	CuI+HBT	45.7	99.0

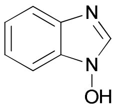
[a] Reaction conditions: HMF 1.26 g (10 mmol), copper halides 2.0 mmol, HBT 0.1 g (0.75 mmol), in 15 mL of DMSO, under 0.3 MPa of O_2, reaction time 10 h, temperature 130 °C. [b] The results are obtained with internal standard technique by GC. [c] The solution of 30.0% H_2O_2 (2.0 equ.) was used as oxidant. [d] The *t*-BuOOH (2 equ.) was used as oxidant.

In order to reveal the influence of redox mediator on the oxidation of HMF, several typical mediators including NHPI, TEMPO, NMO, DDQ and $NaNO_2$ are chosen and used in the CuI-catalyzed oxidation of HMF with dioxygen. As shown in Table 2, it is found that a 52.0% and 95.1% conversion was obtained in DMSO when NHPI and TEMPO was added. Besides, the conversion of HMF was respectively 36.4%, 49.3% and 50.2% in the presence of CuI-NMO, CuI-DDQ and CuI-$NaNO_2$ catalytic system. Considering the efficiency and enconomy, HBT is the most promising as a mediator although the promotion of TEMPO is comparable to that of HBT (the price of TEMPO is more expensive than that of HBT in the market). Furthermore, different solvents including NMP, CH_3CN, γ-butyrolactone, n-butanol, toluene, THF, DMAc and DMF have also been employed in the aerobic oxidation of HMF catalyzed by the CuI-HBT system (Table 2). Herein, a 37.6% or 50% conversion of HMF is obtained when NMP or CH_3CN was employed as the solvent. Otherwise, the conversion of HMF was 30% or 45.1% in γ-Butyrolactone or n-Butanol solvent. However, 82.6% and 18.5% conversion were obtained in toluene and THF solvent. In addition, a 58.7% or 55.4% conversion of HMF is obtained when DMAc or DMF was used as the solvent. It can be seen that the DMSO and toluene as the solvent are superior to other solvents (NMP, CH_3CN, γ-butyrolactone, THF and DMF, etc.), which is probably due to oxidation reaction being more easily performed and the produced DFF is more stable in them.

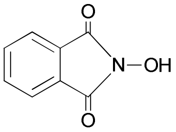
Table 2. Oxidation of HMF with redox mediator in different solvents [a].

Entry	Catalyst system	Solvent	Conversion (%) [b]	Selectivity (%) [b]
1	CuI+NHPI	DMSO	52	94.0
2	CuI+TEMPO	DMSO	95.1	97.0
3 [c]	CuI+NMO	DMSO	36.4	92.0
4 [c]	CuI+DDQ	DMSO	49.3	90
5	CuI+$NaNO_2$	DMSO	50.2	92.0
6	CuI+HBT	NMP	37.6	94.0
7 [d]	CuI+HBT	CH_3CN	50	96.0
8	CuI+HBT	γ-Butyrolactone	30	94.0
9 [d]	CuI+HBT	n-Butanol	45.1	92.0
10	CuI+HBT	Toluene	82.6	99.0
11	CuI+HBT	THF	18.5	92.0
12	CuI+HBT	DMAc	58.7	96.0
13	CuI+HBT	DMF	55.4	98.0

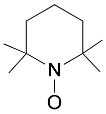
[a] Reaction conditions: HMF 1.26 g (10.0 mmol), CuI 0.38 g (2.0 mmol), 0.75 mmol mediator, in 15 mL solvent, under 0.3 MPa of O_2, at 130 ºC, for 10 h; the corresponding structure of mediator is given as follows:



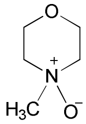
HBT



NHPI



TEMPO



NMO

;

[b] The results are obtained by GC with internal standard technique. [c] The amount of the used additive is 9.0 mol%. [d] The amount of the used CuI is 15.0 mol%.

Figure 1 shows the effect of different amounts of CuI on the oxidation of HMF. It is seen that both the conversion and GC yield are gradually increased along with the amount of CuI being increased from 5.0 mol% to 20.0 mol%. However, the selectivity of HMF almost kept unchanged. The maximum conversion and yield of DFF is 93.2% and 92.3% in the presence of 20.0 mol% CuI catalyst, respectively. When the amount of CuI was further increased to 30.0 mol%, the GC yield is decreased appreciably although the conversion was further elevated. Thus, it can be concluded that the suitable amount of CuI is 20.0 mol% for the oxidation of HMF with dioxygen as oxidant.

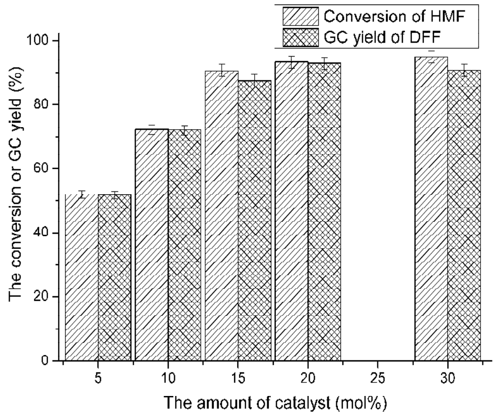


Figure 1. The effect of the amount of CuI for the oxidation of HMF (Reaction conditions: HMF 1.26 g, a certain amount of CuI, HBT 0.1 g, in 15 mL DMSO, under 0.3 MPa of O_2, at 130 ºC, for 10 h).

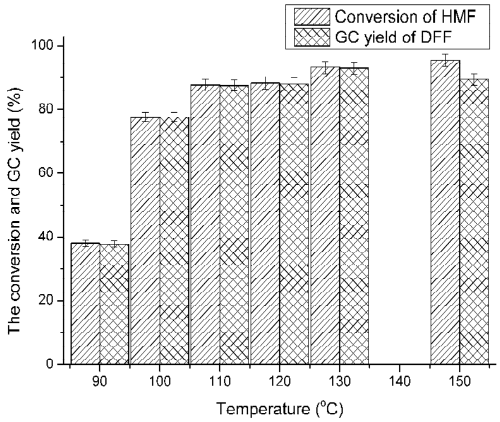


Figure 2. The effect of reaction temperature in the oxidation of HMF (Reaction conditions: HMF 1.26 g, a certain amount of CuI, HBT 0.1 g, in 15 mL DMSO, under 0.3 MPa of O_2, at 130 ºC, for 10 h).

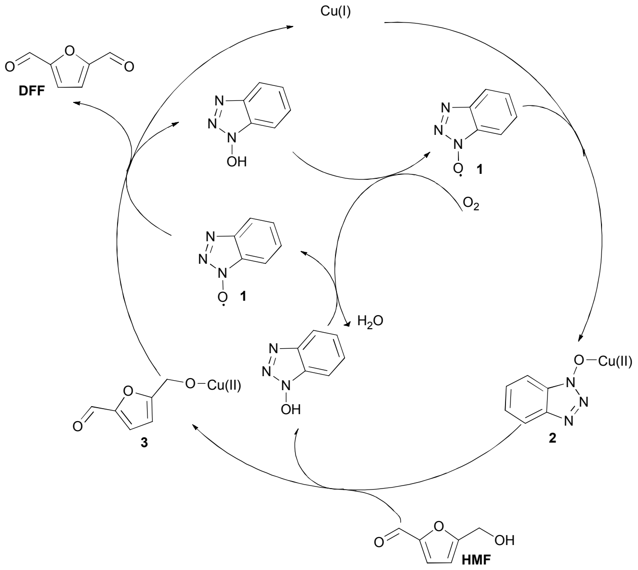
The effect of reaction temperature is investigated and presented in Figure 2. It is seen that the conversion of HMF and GC yield of DFF increases from 90 ºC to 130 ºC; however, the GC yield decreases when the oxidation was carried out at 150 ºC although the conversion was increased. This should be attributed to the occurrence of side reaction and the low DFF selectivity.

In the following, several parameters were investigated about the reaction mechanism and the results are presented in Table 3. It is found that the conversion of HMF was decreased to 84.2% in the presence of hydroquinone (entry 1), which confirmed the reaction contains a free radical pathway in the oxidation. However, the Cu complexing catalysis can also push forward the proceeding of oxidation, which is verified based on the oxidation of HMF in the presence of CuI-benzotriazole catalyst system. Therein, a 62.4% conversion and 93% selectivity for DFF was obtained at 130 °C for 10 h (entry 2). In addition, it was found that a 55.3% or 58.1% conversion was got from the oxidation of HMF with CuI-NHPI-hydroquinone or CuI-hydroquinone system, respectively (entries 3 and 4). These data proved that the whole reaction contains the synergy of radical process and Cu complexing catalysis during the oxidation of HMF. Moreover, the Cu complexing catalysis should be dominant in the oxidation reaction.

Table 3. The investigation on the oxidation mechanism of HMF by CuI [a].

Entry	Catalysts	Additive	Conversion (%) [b]	Selectivity (%) [b]
1	CuI+HBT	Hydroquinone	84.2	99.0
2	CuI+ benzotriazole	-	62.4	93.0
3	CuI+NHPI	Hydroquinone	55.3	98.0
4	CuI	Hydroquinone	58.1	97.0

[a] Reaction conditions: HMF 1.26 g (10.0 mmol), CuI 0.38 g (2.0 mmol), 0.75 mmol mediator, in 15 mL DMSO, under 0.3 MPa of O_2, at 130 ºC, for 10 h; [b] The data were obtained by GC with internal standard method.



Scheme 2. Possible reaction mechanism for the aerobic oxidation of HMF.

Based on the above results and experimental phenomena, a possible reaction mechanism is proposed for oxidation of HMF (shown in Scheme 2). Firstly, a mutual function comes forth between the CuI, HBT and oxygen molecule, a nitroxyl radical (**1**) and an active complex (**2**) is generated in sequence. The following step involves the cracking of O-H bond through transferring of hydrogen atom between HMF molecule and the active complex (**2**), in which Cu(II)-HMF complex (**3**) and HBT molecule can be produced. Finally, with the assistance of the nitroxyl radical (**1**), the C-H bond of the Cu(II)-HMF complex is cleavaged through losing the hydrogen and the Cu(I) cation is obtained again. Then, the next catalytic cycle occurs with another molecular HMF and oxygen. Further investigations about direct capture of reaction intermediates are underway.

Conclusions

In summary, we have developed a new catalytic system for aerobic oxidation in the presence of CuI and HBT. This process allows efficient and selective oxidation of HMF to produce DFF under mild conditions, which will provide a promising ulitization on the application of biomass-derived platform compounds.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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