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Catalytic Upgrading of Biomass-Derived 5-Hydroxymethylfurfural Into Value-Added Products Using Dual Nitrogen-Promoted Cu Catalysts

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ABSTRACT

The oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-diformylfuran (DFF) is a vital reaction for transforming biomass-derived intermediates into high-value chemicals. Herein, a Cu-based co-catalytic system combined with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was developed to utilize molecular oxygen as a green oxidant. Interestingly, such as CuI/TEMPO system can be further enhanced using nitrogen-containing promoters (NCPs) for oxidative conversion. Specifically, 2,2'-bipyridyl (BP) and 1-methylimidazole (MI) are particularly selected as dual NCPs. While HMF could be successfully oxidized to DFF, HMF conversion could be substantially enhanced in the presence of BP and MI, possibly because BP and MI could stabilize Cu species and transform it to become more reactive intermediates for oxidizing HMF. Besides, HMF oxidation to DFF can be further improved at an elevated temperature for a relatively short reaction time (< 10 minute). CuBr was also proven as the more favorable Cu salt for HMF oxidation in comparison with CuCl and CuI. CuI/TEMPO/BP/MI can lead to a much higher yield of DFF (93%) than most reported processes at a much shorter time, and CuI/TEMPO/BP/MI is also reusable for HMF oxidation to DFF.

Keywords: 5-Hydroxymethylfurfural, 2,5-Diformylfuran, Cu Catalyst, TEMPO, Bipyridyl Promoter.

INTRODUCTION

For establishing a sustainable system of resources, valorizing lignocellulos-derived molecules into value-added products has been an important direction of research and development. A wide range of compounds can be derived from lignocellulosic biomass; however, 5-hydroxymethylfurfural (HMF) is especially appealing because it originates directly from the carbohydrate portion of cellulose, a plentiful and renewable resource. A noteworthy feature of HMF lies in its oxidative transformability, enabling the formation of various functional products. Among them, 2,5-diformylfuran (DFF) has gained prominence as a crucial precursor in the manufacture of specialty chemicals and drug intermediates[1-4].

The conversion of HMF to DFF proceeds through oxidation of the hydroxymethyl group to an aldehyde, a transformation that requires precise control over selectivity to ensure efficient valorization. Although hydrogen peroxide (H_2O_2) has been widely employed as an oxidant for biomass-derived substrates, its non-recyclable nature and limited selectivity render it less practical for sustainable processes[5-8], usage of H_2O_2 frequently causes low selectivities and yields of target products. Moreover, H_2O_2 is non-recyclable and continuous consumption of stoichiometric amounts of oxidants is necessitated, making H_2O_2-based oxidation approaches less practical and sustainable.

Recently, more sustainable processes, which directly utilize oxygen molecules as oxidants for oxidizing organics (e.g., alcohols), receive increasing attention[9-12]. In particular, the combination of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and CuI, which efficiently activates molecular oxygen, has emerged as an effective approach for catalytic oxidation of alcohol substrates[13-15]. Such as CuI/TEMPO catalytic system would be useful for catalyzing oxidation of HMF to value-added products[16-20].

Moreover, previous studies found that addition of nitrogen-containing compounds in the system of CuI/TEMPO could improve oxidation of alcohols, and thus these nitrogen-containing compounds were further named as nitrogen-containing promoters (NCPs). In particular, Hansen *et al.,* attempted to screen different NCPs for CuI/TEMPO and found that various NCPs (e.g., ethylendiamine, bis(aminoethyl)amine, tris(aminoethyl)amine, 2,2'-bipyridyl (BP) and dimethylaminopyridine) were useful for promoting HMF conversion[21]. While these NCPs seemed useful, these NCPs were employed individually. However, a few recent studies further reported that incorporation of dual NCPs of BP and 1-methylimidazole (MI) would benefit the CuI/TEMPO system and enhance oxidation of alcohols[13,16-18,22,23].

EXPERIMENTAL

Materials

All reagents used in this study were of analytical grade and utilized without further purification.Copper(I) halides (CuI 98%, CuBr 98%, CuCl 97%), dimethyl sulfoxide (DMSO), and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO, 98%) were obtained from Sigma-Aldrich (USA). The nitrogen-containing ligands 2,2'-bipyridyl (BP, >99%) and 1-methylimidazole (MI, 98%) were supplied by Acros Organics (USA).Deionized water and analytical-grade isopropanol were employed throughout all experiments.

Aerobic oxidation of HMF using CuI/TEMPO

The aerobic oxidation of HMF was performed in isopropanol following the general procedure established in our previous study on Cu-based catalytic systems[24].Initially, a 0.5 mg mL^{-1} HMF solution was prepared, into which 0.25 mmol of CuBr, BP, and TEMPO, along with 1 mmol of MI, were added sequentially. The reaction mixture was then heated to the desired temperature under continuous stirring. At specific time intervals, aliquots (0.5 mL) were withdrawn, filtered through a 0.22 μm nylon syringe filter, and analyzed using HPLC equipped with a UV–Vis detector (HPX-87H column). The mobile phase consisted of 5 mM H_2SO_4 in deionized water with a flow rate of 0.8 mL minute^{-1}.

Chemical conversion and selectivity were calculated using standard definitions reported previously[25]:

$$Conversion(\%) = \frac{\text{Consumed HMF}}{\text{Total HMF}} \times 100\% \qquad (1)$$

$$Selectivity\ for\ DFF(\%) = \frac{\text{DFF (mol)}}{\text{Consumed HMF (mol)}} \times 100\% \qquad (2)$$

$$Yield(\%) = \frac{\text{DFF (mol)}}{\text{Total HMF (mol)}} \times 100\% \qquad (3)$$

RESULTS AND DISCUSSIONS

Cu-catalyzed Aerobic oxidation of HMF

A control experiment was first conducted using TEMPO as the sole oxidant to elucidate its intrinsic activity toward HMF oxidation. As shown in Fig. 1(a), only trace conversion was observed, confirming that TEMPO alone cannot effectively transform HMF into DFF. The addition of CuBr significantly enhanced the reaction performance, leading to 43% HMF conversion and a corresponding DFF yield of 34.4%. This result confirms that Cu facilitates the conversion of HMF to DFF through the formation of reactive copper intermediates[16-18]. Nevertheless, when BP was present, the conversion of HMF was substantially increased to 90% and the yield was also significantly raised up to 70%, demonstrating that the addition of BP considerably improved the conversion of HMF to DFF, possibly because BP would coordinate with CuI and sustain the catalytic activity of CuI[16-18]. This confirmed the favorable role of NCP in oxidation of HMF. Introducing 1-methylimidazole (MI) into the CuI/TEMPO system drastically boosted the catalytic efficiency, yielding complete transformation of HMF and a DFF yield of 80%. The enhanced performance suggests a cooperative role between BP and MI, where the two nitrogen ligands coordinate simultaneously with copper centers. This dual coordination not only stabilizes the metal species but also facilitates the formation of Cu–OH intermediates, which are recognized as highly reactive species for DFF production (Figure 2)[16-18].

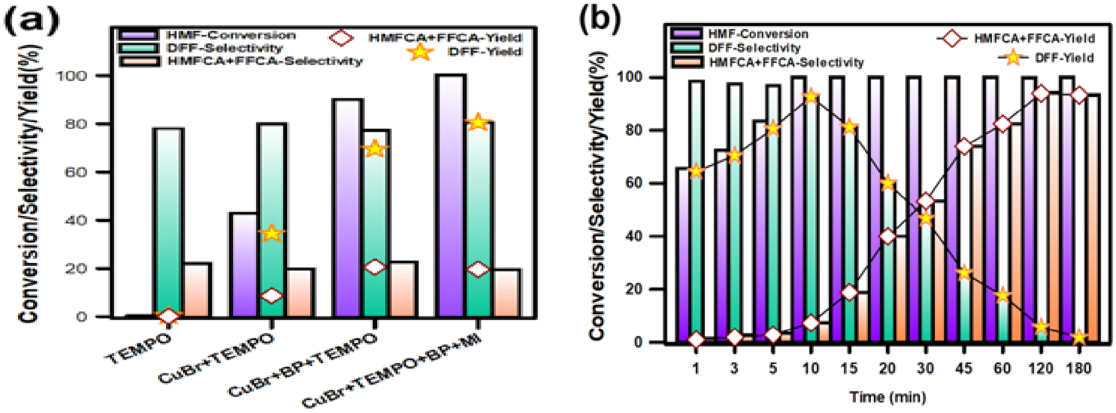

Fig. 1(a). Comparative performance of TEMPO, CuI (with BP/MI), and CuI/TEMPO catalysts for the oxidation of HMF to DFF (reaction time = 10 minute). (b). Variation of HMF conversion with reaction time in the CuI/TEMPO system (10 mL solvent, 5 mg HMF, 0.25 mmol TEMPO, 0.25 mmol catalyst, 30°C)

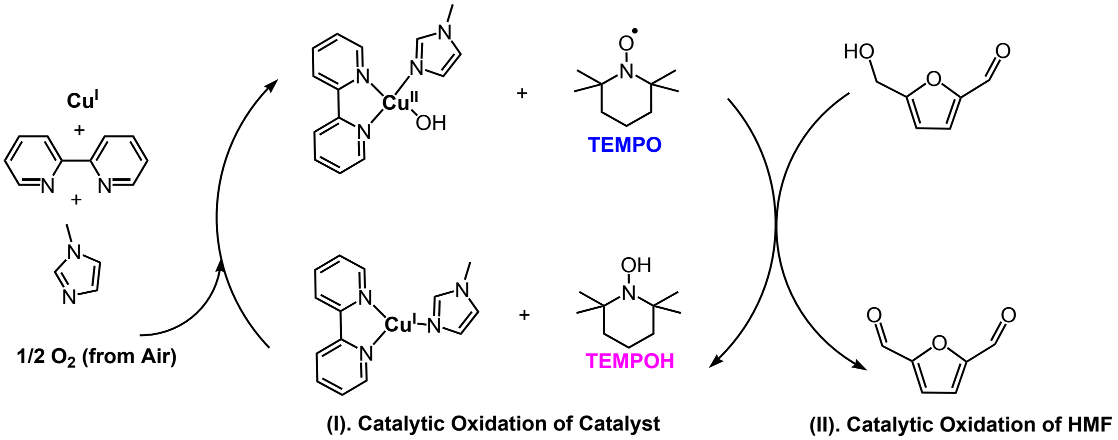

Fig. 2. *Mechanistic illustration* of the aerobic oxidation of HMF catalyzed by the CuI/TEMPO/BP/MI co-catalytic system

Another interesting feature in Fig. 1(a) was that not only DFF was produced from HMF conversion but also HMFCA and FFCA would be detected even in the case of CuI/TEMPO/BP/MI, probably due to the over-oxidation of DFF. To elucidate the time-dependent behavior of the catalytic system, the oxidation of HMF and the formation of DFF, HMFCA, and FFCA were monitored as a function of reaction duration. The corresponding conversion data, presented in Fig. 1(b), reveal the evolution of HMF oxidation over 1–180 min at 30°C under ambient conditions. With the reaction time proceeded, HMF conversion efficiency gradually reached 100% within 10 min and the selectivity of DFF remained higher than 90% throughout first 10 minute. However, DFF selectivity gradually decreased as amounts of HMFCA and FFCA became much higher correspondingly. At a longer reaction time (>30 min), HMFCA and FFCA became dominant products because DFF might be over-oxidized. At 180 min, almost HMF was completely transformed to HMFCA/FFCA eventually, suggesting that HMF conversion required facile control of reaction time even though CuI/TEMPO/BP/MI was promising to boost conversion of HMF.

Temperature-Dependent Behavior of HMF Oxidation in the CuIBr/TEMPO Catalytic System

While HMF oxidation by CuI/TEMPO can be achieved at ambient temperature, temperature may influence HMF oxidation. The catalytic performance of the CuI/TEMPO/BP/MI system was evaluated under different thermal conditions (30–50°C) to examine the temperature effect on HMF oxidation. As shown in Fig. 3, the conversion of HMF increased progressively with temperature, and a pronounced improvement was observed when the temperature rose from 30 to 40°C, particularly within the first 1–5 min of reaction. As the corresponding selectivity for DFF at 1~5 min remained relatively high, the yield of DFF was noticeably increased.

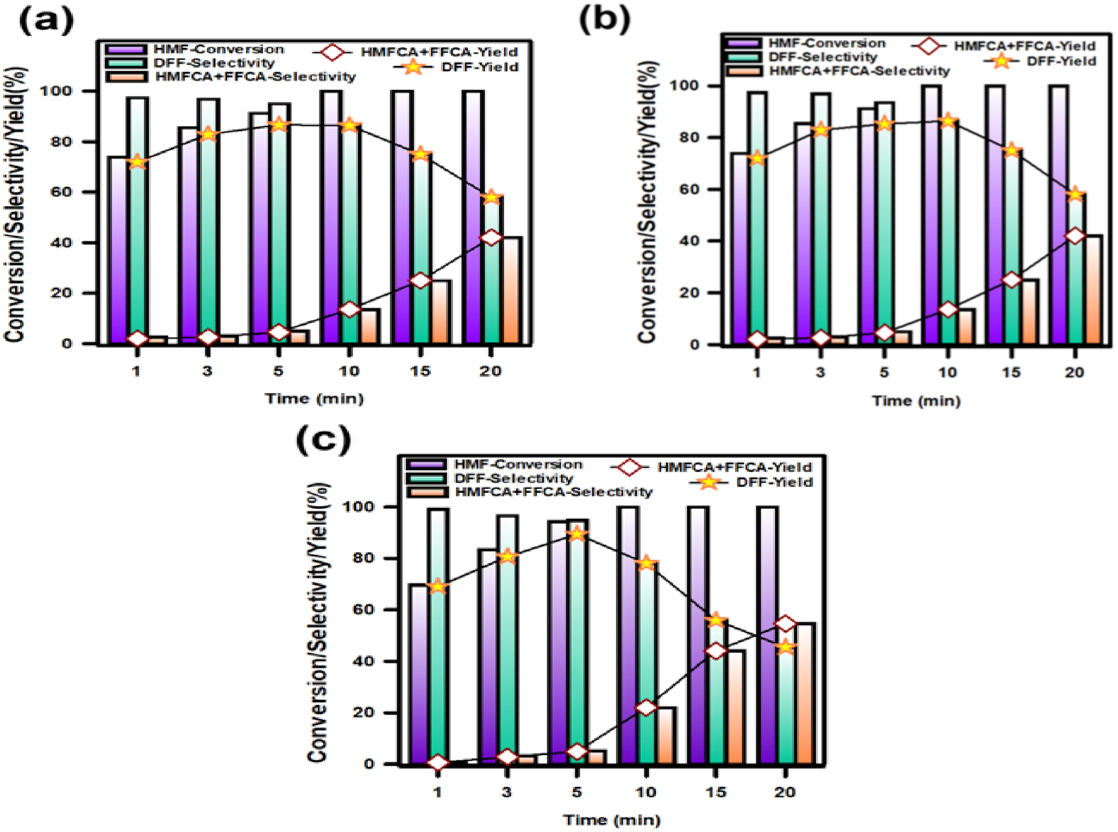

Fig. 3. Temperature-dependent behavior of HMF oxidation at (a) 30°C, (b) 40°C, and (c) 50°C. Experimental parameters: 10 mL solvent, 5 mg HMF, 0.25 mmol TEMPO, and 0.25 mmol catalyst

Such a feature was also observed in the case of HMF oxidation at 50ºC and the yield of DFF was further enhanced at the reaction time shorter than 10 minute. Higher temperatures enhanced DFF yield by increasing HMF conversion.Nonetheless, as the reaction time was extended, the selectivity for DFF was gradually decreased and the production of HMFCA and FFCA was increased at 40°C. The temperature effect became increasingly prominent at 50°C, implying that extended reaction periods at high temperature could cause over-oxidation and diminish DFF selectivity. Accordingly, maintaining short reaction durations (≤ 10 min) at moderately elevated temperature (~50°C) was found to be the most favorable condition for maximizing DFF yield.

Evaluation of Cu and TEMPO Concentration Effects in the Catalytic Oxidation of HMF

The aforementioned results validated that HMF could be successfully converted to DFF by CuI/TEMPO/BP/MI. As Cu and TEMPO played catalytic roles in such a reaction, effects of their dosages on HMF oxidation were further examined to elucidate respective contributions of Cu and TEMPO. Fig. 4 (a) reveals that when the dosage of Cu increased from 0.15 to 0.25 mmol with a fixed amount of TEMPO, the conversion slightly increased while the selectivity for DFF remained comparable, making the yield of DFF increase noticeably. A further increase in Cu concentration above 0.25 mmol led to a modest decline in both conversion and selectivity, which suggests that overloading the catalyst with Cu may disrupt the optimal balance of active sites and consequently impair reaction performance. Meanwhile, the effect of TEMPO dosage was also studied by changing the dosage of TEMPO with a fixed dosage of Cu. Fig. 4 (b) shows that when the TEMPO dosage increased from 0.15 to 0.35 mmol, the conversion of HMF also increased notably; However, the selectivity for DFF gradually decreased.

Furthermore, both the dosages of Cu and TEMPO were varied from 0.15 to 0.35mmol to examine the quantities of Cu and TEMPO on HMF oxidation in Fig. 4(c). Similarly, when the dosages of Cu and TEMPO increased from 0.15 to 0.25 mmol, the conversion of HMF increased from 93.4 to 100% and the yield of DFF also increased from 90 to 93% correspondingly. Nevertheless, once the dosages of Cu and TEMPO exceeded 0.25 mmol, the yield of DFF decreased from 93 to 84.2% because of relatively low selectivities for DFF. These results further validated that the optimal dosages of Cu and TEMPO would be 0.25 mmol and excessive dosages might cause over-oxidation of DFF.

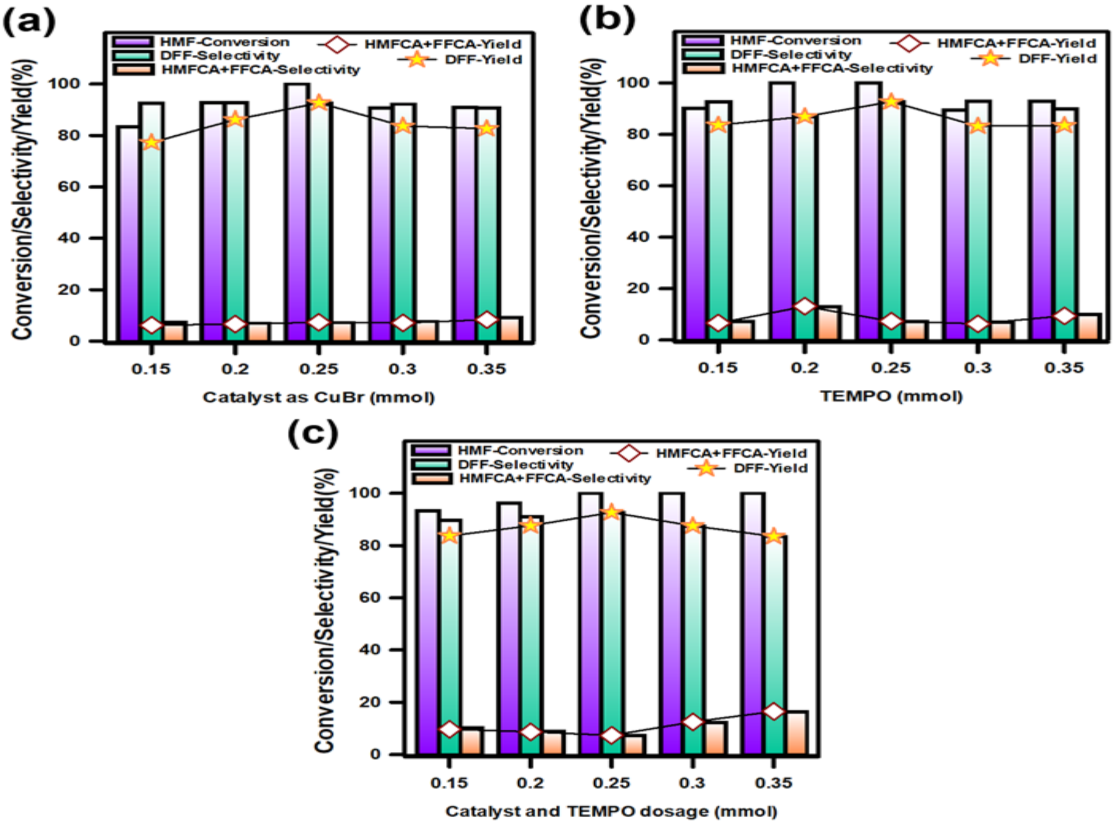

Fig. 4. Effect of (a). CuIBr (with BP/MI) dosage (TEMPO dosage = 0.25 mmol), (b). TEMPO dosage and (c). CuIBr (with BP/MI) and TEMPO dosage (solvent = 10 mL, HMF = 5 mg, T = 30°C, t = 10 minute)

Comparative Evaluation of Copper Halide Precursors in the CuI/TEMPO-Catalyzed HMF Oxidation

While CuI is commonly employed as an effective copper source in the CuI/TEMPO oxidation system, its halide analogues (CuCl and CuBr) were also investigated to determine how the choice of salt affects catalytic performance. As displayed in Fig. 5, all three salts produced comparable HMF conversion and DFF selectivity, yet CuBr yielded slightly higher activity. This enhancement may stem from differences in halide coordination and solubility, which influence the formation and transformation of copper intermediates during the oxidation process[18].

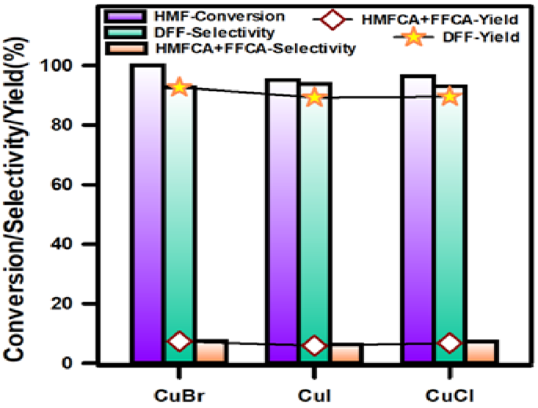

Fig. 5. Effect of CuI species on oxidative conversion of HMF (solvent = 10 mL, HMF = 5 mg, TEMPO = 0.25 mmol, catalyst = 0.25 mmol, t = 10 minute)

Moreover, interactions between different CuI salts and TEMPO could be also altered, influencing oxidation efficiencies of TEMPO 26. Therefore, previous studies observed the similar tendency when using CuBr and CuCl for oxidation of alcohols and found that CuBr exhibited a higher conversion efficiency[17,18]. Thus, CuBr seems as a more favorable CuI species for HMF oxidation because of higher conversion efficiencies, selectivities and yield.

Furthermore, to understand the competitiveness of the combination of CuI/TEMPO/BP/MI for HMF oxidation, HMF conversion efficiencies by various approaches reported in previous studies as shown in Table 1. In comparison with other processes, CuI/TEMPO/BP/MI certainly exhibited noticeably a higher yield of DFF. Most importantly, the reaction time of HMF oxidation by CuI/TEMPO/BP/MI can be as short as 10 min or even shorter for effective HMF conversion. This rapid reaction highlights the kinetic superiority of the dual-promoted Cu/TEMPO system for selective conversion of HMF to DFF.

Catalyst Stability and Reusability of CuIBr/TEMPO during HMF Oxidation

While CuI/TEMPO/BP/MI is a homogeneous catalytic system, it would be interesting to explore whether the mixture of CuI/TEMPO/BP/MI could be reusable for HMF oxidation. To this end, CuI/TEMPO/BP/MI remained in the reactor after HMF oxidation and an addition of fresh HMF was poured into the reactor for a subsequent experiment. Fig. 6 illustrates that the CuI/TEMPO/BP/MI catalyst retained its oxidation efficiency after repeated use, achieving effective HMF conversion to DFF over four consecutive cycles. The formation of intermediates such as HMFCA and FFCA remained minimal, indicating excellent catalyst stability and reusability. This result confirmed that CuI/TEMPO/BP/MI could be reusable and their catalytic activities can be remained and stable.

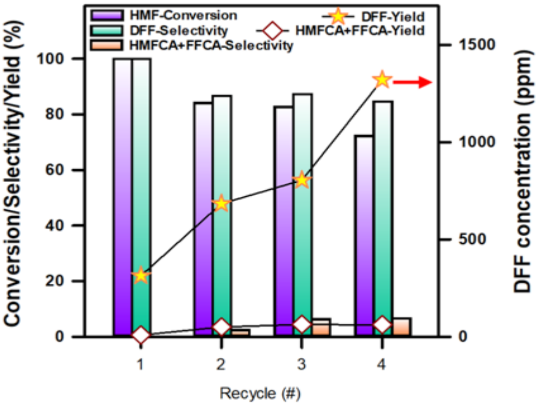

Fig. 6. Evaluation of CuIBr/TEMPO catalyst stability and reusability in the oxidation of HMF to DFF. Reaction conditions: 10 mL solvent, 5 mg HMF, 0.25 mmol TEMPO, 0.25 mmol catalyst, and 10 min reaction time

Table 1: Summary of Catalytic Performance for HMF Oxidation to DFF Using Different Catalyst Systems

Catalyst	Oxidant	Solvent	T(°C)	Time	O_2	Conversion(%)	Selectivity(%)	Yield(%)	Reference
CuBr/TEMPO	Air	DMSO	RT	10 m	-	100	93	93	This study
$Cu(NO_3)$	O_2	CH3CN	80	24 h	1.0 MPa	90.6	99	89	27
4-Acetamido-TEMPO	O_2	EtOAC	40	2 h	10 mL/min	100	89	89	28
CuCl/TEMPO	O_2	Acetonitrile	RT	24 h	0.1MPa	44	97	42	29
CuI/TEMPO	O_2	DMSO	130	10 h	0.3MPa	95.1	97		30
Ru/C	Air	MTBE	80	1 h	2.0MPa	54.5	-	43.7	31
Pd/C	Air	MTBE	80	1 h	2.0MPa	19.4	-	8.8	
Pt/C	Air	MTBE	80	1 h	2.0MPa	28.5	-	1.3	
Cs/MnOx	O_2	DMF	100	10 h	1.0MPa	76.8	98.1		32
MnO_2	O_2	DMF	100	10 h	1.0MPa	2.4	89.8		
Ru/AC	H_2O_2	H2O	75	1 h	-	94	-	14	3
$Co_{3.3}Ce_{3.3}Ru_{3.3}$	H_2O_2	MIBK	120	12 h	-	98.7	80.2	79.2	33

CONCLUSION

In this study, HMF was successfully oxidized to DFF and further enhanced by dual NCPs, BP and MI. The presence of BP and MI probably stabilized Cu species and maintained its catalytic activities for oxidizing HMF. HMF oxidation to DFF can be further improved at an elevated temperature (e.g., 50°C) for a relatively short reaction time (<10 minute). While higher dosages of CuI/TEMPO increased conversion of HMF, excessive dosages would cause negative effects (i.e., over-oxidation of DFF). CuBr was also proven as the more favorable Cu salt for HMF oxidation in comparison with CuCl and CuI. More importantly, CuI/TEMPO/BP/MI can be reusable and continuously employed for HMF oxidation to DFF. The results highlight the CuI/TEMPO/BP/MI system as an effective and durable co-catalytic framework, offering strong promise for the selective transformation of HMF into DFF under mild aerobic conditions.

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Conflict of interest

The authors declare they have no competing interests.

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Author contributions

Jia-Yin Lin: Writing–original draft, Visualization, Formal analysis. Chih-Ying Wang: Methodology, Investigation. Kun-Yi Andrew, Lin: Writing – review & editing, Data curation, Supervision.

Data Availability Statement

All data supporting the findings of this study are available from the corresponding author upon reasonable request.

Ethical Approval Statement

This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent Statement

Not applicable.

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