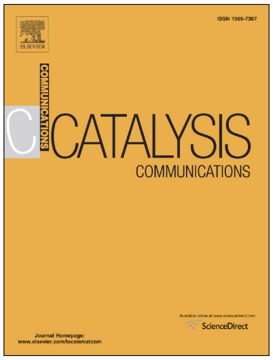

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# Highly Efficient and Selective Oxidation of 5-Hydroxymethylfurfural by Molecular Oxygen in the Presence of Cu-$MnO_2$ Catalyst

**Xinli Tong*, Linhao Yu, Hui Chen, Xuli Zhuang, Shengyun Liao* and Hongge Cui**

*Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, P. R. China;*

*Tel.: +86-22-60214259; Fax: +86-22-60214259;*

*E-mail address: tongxinli@tju.edu.cn; tongxli@sohu.com (X. T.) or mengyunliao@sina.com (S. L.).*

## Abstract

The selective oxidation of 5-hydroxymethylfurfural (HMF) to produce value-added chemicals is a hot topic in the utilization of biomass, in which the development of heterogeneous catalyst and the use of $O_2$ as terminal oxidant is desired. In this work, a series of metal ion-doped $MnO_2$ materials are successfully prepared using liquid precipitation method, and employed as catalysts for the aerobic oxidation of HMF in the alcoholic solvents. As a result, it is found that 86.0% conversion of HMF and 96.1% selectivity of 2, 5-formyl furan (DFF) was obtained under suitable conditions. Moreover, the Cu-$MnO_2$ catalyst can keep a high activity after being recycled five times.

**Keywords**: Oxidation; 5-hydroxymethylfurfural; 2, 5-diformylfuran; Manganese oxide; Biomass transformation

## 1. Introduction

Along with the diminishing fossil fuels and the increasing environmental pollution, the efficient utilization of the renewable biomass has become an attractive hot topic, in which the catalytic synthesis of fine chemicals and liquid fuels from biomass feedstock is being broadly studied [1-4]. With the consideration of downstream chemical processing, the catalytic transformation of 5-hydroxymethl furfural (HMF), a famous platform compound, to the value-added chemical is important in both science and commerce. Thus, much effort has been devoted to the oxidation of HMF to 2, 5-diformyl furan (DFF), 5-formyl-2-furancarboxylic acid (FFCA) and 2, 5-furandicarboxylic acid (FDCA), which can be used for the production of drugs, fungicides, and new functional polymers [5-7]. Thereinto, the oxidation of HMF to DFF is facing to a challenge owing to the poor selectivity and severe reaction conditions. Although the direct oxidation of HMF can be successfully performed with stoichiometric oxidants or the assistance of electrophilic agents [8, 9], the catalytic aerobic oxidation of HMF to prepare DFF is more valuable in the practical application from the viewpoints of economy and sustainability.

Recently, the use of molecular oxygen or air as oxidant was extensively investigated. In the homogeneous catalytic process, the catalytic aerobic oxidation of HMF using a mixed Co/Mn/Zr/Br system has been performed in which a 57% yield of DFF was attained [10]. Ma et al. [11] 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. Besides, our group also found that the homogeneous catalytic oxidation of HMF to produce DFF could be achieved using CuI and 1-hydroxybenzotriazole as the catalysts, in which a 93.2% conversion and 99.0% selectivity of DFF was obtained [12]. However, all these systems have the obvious disadvantage on the separation of product and the recycling of catalyst. So, developing the heterogeneous and efficient solid catalyst for the oxidation of HMF remains an issue of scientific interest at present. In early work, Verdeguer et al. found that a 19% yield of DFF was obtained under a high temperature and neutral pH when Pt/C catalyst was used in the aerobic oxidation of HMF [13]. Moreover, Navarro et al. [14] reported a 50% conversion and 98% selectivity of DFF was obtained for the aerobic oxidation of HMF with vanadyl complexes supported SBA-15 catalyst. Sádaba et al. [15] detected the performance of zeolite-supported vanadia catalysts for the aerobic oxidation of HMF, in which a 99% selectivity of DFF at 84% conversion was obtained. Antonyraj et al. [16] studied the oxidation of HMF with $V_2O_5$/C catalyst, and a 95% conversion in a 96% selectivity of DFF was attained. When polyanline-grafted vanadyl acetylacetonate was used as catalyst for the aerobic oxidation of HMF, a 99.2% conversion and 86.2% yield of DFF was obtained at 110 ºC for 12 h [17]. In addition, Nie et al. [18] reported that the Ru/C catalyst could efficiently promote the oxidation of HMF to prepare DFF with a high yield of about 96% at 110 ºC in toluene. Chen’s group [19] studied the oxidation of HMF with Ru-PVP/CNT catalyst and a 94% yield of DFF with a full HMF conversion was obtained under the suitable conditions. Furthermore, the lipophilic nano-ruthenium catalyst was used to the oxidation of HMF, in which a 94% conversion and 89% selectivity of DFF was attained at 105 ºC for 8 h in methyl isobutyl ketone solvent [20]. Besides, the aerobic oxidation of HMF to DFF was also investigated with manganese oxide octahedral molecular sieve (OMS-2) as the catalyst in which a high yield of 97.2% was attained under 0.5 MPa of $O_2$ in *N*, *N*-dimethyl formamide (DMF) solvent [21]. Moreover, the Ag-OMS-2 was found to exhibit the high catalytic activity in the aerobic oxidation of HMF where a 99% yield of DFF was achieved [22]. Recently, Zhu et al. [23, 24] found that the Au/$MnO_2$ or Au-Pd/$MnO_2$ efficiently catalyzed the oxidation of HMF, in which about 82%

conversion of HMF and 99.0% selectivity of DFF was obtained under the optimal conditions. The above numerous heterogeneous catalysts show good catalytic performance in the aerobic oxidation of HMF in organic solvents; however, the preparation of catalyst was complicate and expensive which is disadvantageous for the application.

Very recently, due to its easy preparation and high electrocatalytic activity, metal ion-doped $MnO_2$ catalyst has been extensively studied [25]. In this work, considering the probable synergistic effect of Cu and $MnO_2$, we employ the Cu-doped $MnO_2$ as heterogeneous catalyst for the oxidation of HMF with molecular oxygen as oxidant. It is found that 86.0% conversion and 96.1% selectivity of DFF was obtained in the presence of Cu(4.8 mol%)-$MnO_2$ catalyst at 140 ºC for 5 h.

## 2. Experimental

### 2.1 The preparation of nano-structured $MnO_2$ catalyst

The aqueous solution (100 mL) of $KMnO_4$ (5.89 g) was added into an aqueous solution (30 mL) of $MnSO_4 \cdot H_2O$ (8.8 g) and concentrated $HNO_3$ (3 mL). Then, the resulting mixture was refluxed at 100 °C for 24 h. Finally, the dark brown solid formed was filtered off, washed with a large amount of water, and dried under open air at 150 °C, affording 7-8 g of nano $MnO_2$ material.

### 2. 2 The preparation of metal ion doped $MnO_2$ catalysts

For the preparation of Cu-doped $MnO_2$ catalyst: firstly, an aqueous solution (100 mL) of $KMnO_4$ (5.89 g) was added into an aqueous solution which contains $MnSO_4 \cdot H_2O$ (8.8 g), a certain amount of $CuSO_4$ and concentrated $HNO_3$ (3 mL). Then, the resulting mixture was refluxed at 100 °C for 24 h. Finally, the dark brown solid formed was filtered off, washed with a large amount of water, and dried under open air at 150 °C, affording Cu-doped $MnO_2$ material which is signified by Cu (x mol%)-$MnO_2$ (x mol% refers the molar ratio of $Cu^{2+}$ and $MnO_2$; if x mol%= 2.4 mol%, x mol% can be left out). Similarly, Cr-$MnO_2$, V-$MnO_2$, Mo-$MnO_2$, Mg-$MnO_2$, Ca-$MnO_2$ or Al-$MnO_2$ catalysts are prepared through $Cr(NO_3)_3$, $NaVO_3$, $K_2MoO_4$, $Mg(NO_3)_2$, $Ca(NO_3)_2$ and $Al(NO_3)_3$ replacing $CuSO_4$ as the doping metal salts.

### 2.3 General procedure for the aerobic oxidation of 5-hydroxymethylfurfural (HMF)

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 methanol (15 mL) solution of HMF (0.252 g, 2.0 mmol) and Cu-$MnO_2$ catalyst (0.05g) 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 140 ºC, and then kept for 5 h. After reaction, the autoclave was cooled and the obtained mixture is analyzed by HPLC and GC-MS instruments after the excess gas is purged (the detection of product is presented in 1.2 and Figure S1 of supporting information).

## 3. Results and Discussion

### 3.1 TEM images

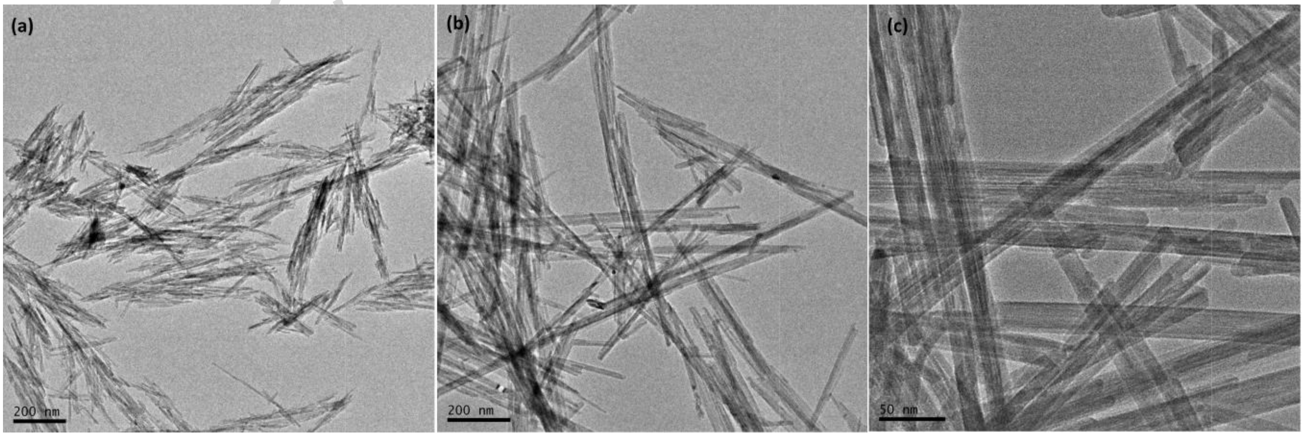


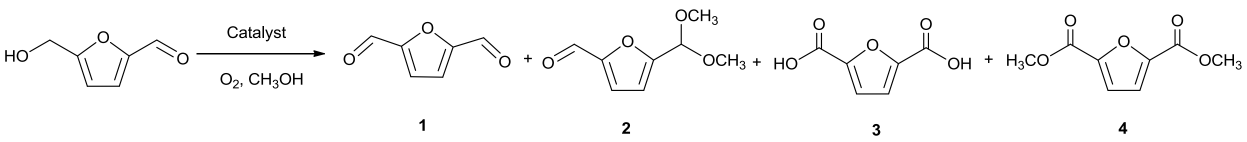
**Figure 1.** TEM images of different catalytic materials [**a**. $MnO_2$; **b** and **c**. Cu (4.8mol%)-$MnO_2$].

In order to reveal the structure and morphology of catalytic materials, the TEM characterization was performed. As shown in Figure 1a, the pure $MnO_2$ material possesses a fibrous morphology. The average length and width of the fibers were 500 ± 100 nm and 20 ± 5 nm, respectively. While, the fibrous morphology of Cu (4.8 mol%)-$MnO_2$ material is more regular which trends to the formation of nanowire structure (Figures 1b and 1c). Correspondingly, the average length and width of the fibers were 90 ± 50 nm and 25 ± 2 nm, respectively. These results indicate that the structure and morphology becomes well-defined after being doped by 4.8 mol% $Cu^{2+}$ ion. Moreover, it can be inferred that the substitutional doping of Cu ion into the $MnO_2$ lattice, combined with the results of the XRD detection (Figure S2), which is consistent with the conclusion of the reference [25].

### 3.2 SEM images

In the following, the catalytic materials are characterized by the SEM technique. Figure S3 shows the SEM images of $MnO_2$, Cu(2.4 mol%)-$MnO_2$, Cu(4.8 mol%)-$MnO_2$,Cu(6.0 mol%)-$MnO_2$, Cu(7.2 mol%)-$MnO_2$ and Cu(9.6 mol%)-$MnO_2$, respectively. As a result, it is found that there exists the irregular surface in the obtained pure $MnO_2$ material. Along with the increase of doping amount of $Cu^{2+}$ ion from 2.4 mol% to 9.6 mol%, the material surfaces become more and more regular in which the surface of Cu(4.8 mol%)-$MnO_2$ is loose and similar to nanowire. However, when the doping Cu amount is larger and larger, the material surface is tighter and tighter although the formation of more nanowires was achieved. These phenomena also confirm the relationship of the surface area of materials and the doping Cu amount.

### 3.3 The oxidation of 5-hydroxymethylfurfural (HMF) with various catalysts



**Scheme 1.** The reaction equation for selective oxidation of HMF with molecular oxygen

**Table 1.** The oxidation of HMF to DFF with different catalysts [a].

| Entry | Catalysts | Conv.(%)[b] | Product distribution (%) [b] | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | **1** | **2** | **(1+2)** | **3** | **4** | Others |
| 1 | $MnO_2$ | 57.9 | 51.9 | 18.3 | 70.2 | 4.3 | 14.6 | 10.9 |
| 2 | Cu-$MnO_2$ | 74.8 | 50.9 | 17.6 | 68.5 | 1.0 | 18.7 | 11.8 |
| 3 | Cr-$MnO_2$ | 77.6 | 30.7 | 20.1 | 53.8 | 6.8 | 21.3 | 18.1 |
| 4 | V-$MnO_2$ | 67.9 | 45.8 | 12.3 | 58.1 | 1.2 | 26.5 | 14.2 |
| 5 | Mo-$MnO_2$ | 56.1 | 46.4 | 16.2 | 63.6 | 7.1 | 24.6 | 4.7 |
| 6 | Mg-$MnO_2$ | 54.5 | 40.3 | 8.9 | 49.2 | 5.9 | 19.8 | 25.1 |
| 7 | Ca-$MnO_2$ | 51.5 | 45.7 | 12.5 | 58.2 | 4.6 | 16.7 | 20.5 |
| 8 | Al-$MnO_2$ | 39.5 | 43.5 | 13.6 | 57.1 | 7.4 | 26.8 | 8.7 |

[a] Reaction conditions: HMF 0.2520 g (2 mmol), the catalyst 0.05 g, in 15 mL of methanol, under 0.3 MPa of $O_2$, time 5 h, temperature 140 ºC. [b] The results are obtained by GC and HPLC with the internal standard technique.

Initially, the oxidation of HMF, as shown in Scheme 1, is performed in methanol solvent under 0.3 Mpa of $O_2$ using different metal ion-doped maganease oxides as catalysts. The obtained data are summarized in Table 1. It is found that the conversion of HMF and the selectivity of **1** was respectively 57.9% and 70.2% with the $MnO_2$ catalyst at 140 ºC for 5 h (entry 1). While, the conversion was elevated to 74.8%, 77.6% or 67.9% when Cu-$MnO_2$, Cr-$MnO_2$ or V-$MnO_2$ were used as the catalysts, respectively (entries 2, 3 and 4), in which the selectivity of **1** was 68.5%, 53.8% or 51.8%, respectively. Moreover, it is also found that the selectivity of **3** was respectively increased to 18.7%, 21.3% or 26.5% from the original 14.6%. Furthermore, the catalytic performance of

Mo-$MnO_2$, Mg-$MnO_2$ and Ca-$MnO_2$ were investigated, and the conversion of HMF was respectively 56.1%, 54.5% and 51.5%, in which the selectivity of **1** was 63.6%, 49.2% and 58.3%, respectively. Besides, a only 39.5% conversion of HMF and 57.1% selectivity of **1** was obtained in the presence of Al-$MnO_2$ catalyst. These data exhibit that the doping of $Cu^{2+}$, $Cr^{3+}$, and $V^{3+}$ may efficiently promote the aerobic oxidation of HMF in which the Cu-$MnO_2$ catalyst is more suitable for the production of **1** in methanol solvent (the oxidation states of Mn, Cu, Cr and V have been confirmed by the representive XPS data in the Figure S4 of supporting information). It can be attributed that the substitutional doping of Cu ion into the $MnO_2$ lattice is beneficial to the exchange of $Mn^{4+}$ and $M^{3+}$ or the shift of lattice oxygen. Besides, related to the characterization of different catalysts, it can be seen that the activity of catalytic materials is closely associated with the BET surface area (the data are given in Table S1 in the supporting information). Therein, the doping of $Cu^{2+}$, $Cr^{3+}$, and $V^{5+}$ lead to the surface area of $MnO_2$ increasing from 88.9 $m^2 \cdot g^{-1}$ to 100.9, 102.5 and 99.3 $m^2 \cdot g^{-1}$, respectively.

### 3.4 The effect of reaction medium in the aerobic oxidation of HMF with Cu-$MnO_2$ catalyst

**Table 2.** Oxidation of HMF with Cu-$MnO_2$ catalyst in different solvents [a].

| Entry | Solvents | Conversion (%)[b] | Product distribution (%) [b] | | |
|---|---|---|---|---|---|
| | | | **1**[c] | **3** | Others |
| 1 | ethanol | 72.8 | 89.1 | 3.5 | 7.4 |
| 2 | n-propanol | 71.6 | 74.5 | 16.0 | 9.5 |
| 3 | n-butanol | 70.9 | 73.2 | 14.3 | 12.5 |
| 4 | 1-pentanol | 62.6 | 62.1 | 11.7 | 26.2 |
| 5 | toluene | 50.3 | 72.5 | 8.3 | 19.2 |
| 6 | benzonitrile | 18.5 | 82.1 | 7.2 | 10.7 |
| 7 | water | 30.2 | 64.2 | 25.5 | 10.3 |
| 8 | dichloromethane | 42.1 | 68.3 | 18.5 | 13.2 |
| 9 | acetonitrile | 26.7 | 79.8 | 9.9 | 10.3 |

[a] Reaction conditions: HMF 0.2520 g (2 mmol), the Cu-$MnO_2$ catalyst 0.05 g, in 15 mL of solvent, under 0.3 MPa of $O_2$, reaction time 5 h, temperature 140 ºC. [b] The results are obtained by GC and HPLC with internal standard technique. [c] The selectivity of **1** includes the partial acetal compound.

The effects of reaction media on the selective oxidation of HMF were studied in the presence of the Cu-$MnO_2$ catalyst. As shown in Table 2, it is found that 72.8% and 71.6% conversions as well as 89.1% and 74.5% selectivities of **1** were respectively obtained in ethanol and n-propanol. Besides, the conversion of HMF was respectively 70.9% and 62.6% 5 in n-butanol and 1-pentanol solvent. Furthermore, several organic solvents including toluene, benzonitrile, water, $CH_2Cl_2$ and $CH_3CN$ have also been employed in the aerobic oxidation of HMF with Cu-$MnO_2$ catalyst. As a result, a 50.3%, 18.5% or 30.2% conversion of HMF was obtained in toluene, benzonitrile or water solvent. In addition, a 42.1% and 26.7% conversion was obtained when $CH_2Cl_2$ and $CH_3CN$ were used as the solvent. It can be seen that the ethanol or methanol as the solvent are superior to other solvents (toluene, benzonitrile, water, $CH_2Cl_2$ and $CH_3CN$, etc.), which is probably due to oxidation reaction being more easily performed and the produced DFF is more stable in these alcoholic solvents. Considering the efficiency and enconomy, ethanol is considered as the most promising solvent in oxidation of HMF by molecular oxygen.

### 3.5 The influence of the doping copper (Cu) amount

**Table 3.** The effect of the doping Cu amount on the oxidation of HMF [a].

| Entry | The doping Cu amount | Conv. (%)[b] | Product distribution (%) [b] | | | | |
|---|---|---|---|---|---|---|---|
| | | | **1** | Acetal[c] | **1**+Acetal | **3** | Ester[d] |
| 1 | 0 mol% | 33.6 | 49.6 | 41.3 | 90.9 | 2.1 | 7.0 |
| 2 | 2.4 mol% | 72.8 | 47.5 | 41.6 | 89.1 | 3.5 | 7.4 |
| 3 | 3.6 mol% | 74.8 | 49.3 | 42.5 | 91.8 | 2.9 | 5.3 |
| 4 | 4.8 mol% | 77.7 | 51.2 | 44.2 | 95.4 | 3.2 | 1.4 |
| 5 | 6.0 mol% | 68.7 | 51.5 | 44.6 | 96.1 | 2.8 | 1.1 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 6 | 7.2 mol% | 48.7 | 53.2 | 45.1 | 98.3 | 0.9 | 0.8 |
| 7 | 9.6 mol% | 34.6 | 53.5 | 44.3 | 97.8 | 1.2 | 1.0 |

[a] Reaction conditions: HMF 0.2520 g (2 mmol), the Cu(x mol%)-$MnO_2$ catalyst 0.05 g, in 15 mL of ethanol, under 0.3 MPa of $O_2$, reaction time 5 h, temperature 140 ºC. [b] The results are obtained by GC and HPLC with internal standard technique. [c] The obtained acetal refers to 5-(diethoxymethyl)furan-2-carbaldehyde. [d] The generated ester refers to ethyl 5-formylfuran-2-carboxylate.

In the following, the effect of doping Cu amount on the HMF oxidation was further studied in ethanol. Seen from the Table 3, the doping amount of $Cu^{2+}$ ion was changed from 2.4 mol% to 9.6 mol%. It is found that, along with the doping amount of $Cu^{2+}$ being added from 0 mol% to 4.8 mol%, the conversion of HMF was increased from 33.6% to 77.7% and the selectivity of **1** was also elevated from 90.9% to 95.4%. However, when the doping amount of $Cu^{2+}$ was further elevated to 6.0 mol%, 7.2 mol% and 9.6% mol%, the conversion of HMF was respectively declined to 68.7%, 48.7% and 34.6%, although the selectivity of **1** was still increased a little. Considering to the change of surface area along with the increase of doping amount, in which the surface area of Cu(2.4mol%)-$MnO_2$, Cu(4.8mol%)-$MnO_2$, Cu(6.0mol%)-$MnO_2$, Cu(7.2mol%)-$MnO_2$ and Cu(9.6mol%)-$MnO_2$ is 92.3, 100.9, 83.7, 66.1 and 32.7 $m^2 \cdot g^{-1}$, respectively, which further prove that the surface area of these catalysts play a curial role on their catalytic activities. Accordingly, the best catalyst is Cu(4.8mol%)-$MnO_2$ material. It should be attributed to the cooperation effect of the substitutional doping of Cu ion into the $MnO_2$ lattice and the elevation of surface area.

### 3.6 The effect of the amount of catalyst and the recycling of catalyst

Figure S5 shows the effect of different amounts of catalyst on the oxidation of HMF. It is seen that both the conversion and selectivity of **1** were gradually increased along with the amount of catalyst being increased from 0.025 g to 0.100 g. However, the selectivity of HMF was almost kept unchanged. The maximum data were 86.0% conversion and 96.1% selectivity of **1** where 0.100 g of

Cu (4.8 mol%)-$MnO_2$ was used. When the amount of catalyst was further increased to 0.15 g or more, the selectivity of **1** was decreased appreciably although the conversion was further elevated. In succession, the effects of reaction temperature and time were also studied and the obtained data are indicated in Figure S6 and Figure S7 of the supporting information.

In addition, the recycling of Cu(4.8 mol%)-$MnO_2$ catalyst was examined to study its stability. After the oxidation reaction, the solid catalyst was separated, and washed with anhydrous ethanol, and then dried at 80 ºC for 12 h before being reused in the next run. As shown in Figure S8, it was seen that the conversion of HMF and the selectivity of **1** kept more than 75% even after the Cu(4.8 mol%)-$MnO_2$ material being recycled five times. These results indicated that the catalyst is recyclable and stable in the oxidation of HMF using dioxygen as oxidant.

## 4. Conclusion

In summary, we have developed a new selective and aerobic oxidation of HMF to produce DFF in the presence of a heterogonous Cu-doped $MnO_2$ catalyst. This process allows efficient and selective oxidation of HMF under mild conditions, which will provide a promising aerobic oxidation technique for the sustainable utilization of biomass-derived platform compounds.

## Acknowledgements

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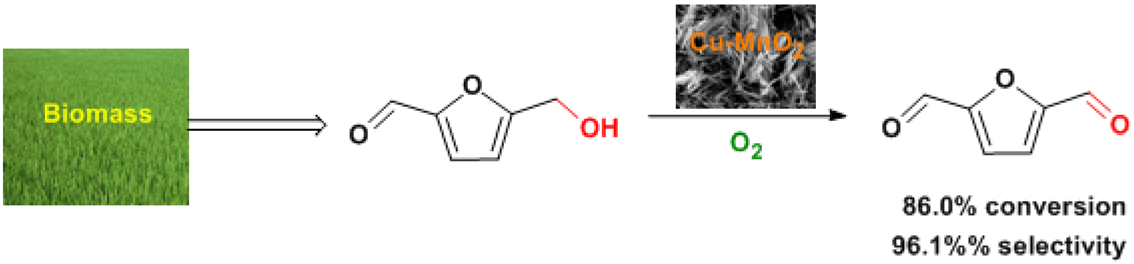
# Graphical Abstract



Highly efficient and selective oxidation of biomass-derived 5-hydroxymethylfurfural with molecular oxygen has been successfully performed in the presence of a heterogeneous Cu-$MnO_2$ catalyst.

# Highlights

- The efficient oxidation of 5-hydroxymethylfurfural is successfully performed.
- Nano-structured Cu-$MnO_2$ is a preferable catalyst in ethanol solvent.
- An 82.6% yield of 2, 5-diformylfuran is obtained under mild conditions.
- The catalyst still keeps a high activity after being recycled for 5 times.