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Original article

Iron-catalyzed selective oxidation of 5-hydroxymethylfurfural in air: A facile synthesis of 2,5-diformylfuran at room temperature

Chi Fang^a, Jian-Jun Dai^b, Hua-Jian Xu^{b,*}, Qing-Xiang Guo^a, Yao Fu^{a,*}

^a Anhui Province Key Laboratory of Biomass Clean Energy, Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

^b School of Medical Engineering Hefei University of Technology, Hefei 230009, China

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ABSTRACT

An iron(III)-catalyzed selective oxidation of 5-HMF to 2,5-DFF in air at room temperature was developed. This approach gives 2,5-DFF with good selectivity and yields. Additionally, a two-step process was developed for the oxidation of 2,5-DFF to 2,5-FDCA at remarkably high substrate concentrations. This work demonstrates unequivocally the great potential of iron as a cheap and earth-abundant catalyst for the development of new protocols for the conversion of biomass to value-added chemicals.

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1. Introduction

The conversion of biomass to chemicals has become an important research area in the field of biomass utilization in recent years [1]. Of particular importance is the transformation of biomass to 5-hydroxymethylfurfural (5-HMF, **1**) [2], which can be obtained easily from cellulose [3] and transformed readily to fuels and other value-added chemicals [4]. As one of the most important derivatives of **1**, 2,5-diformylfuran (2,5-DFF, **2**) has attracted much attention because of its applications in the synthesis of a number of valuable compounds such as pharmaceutical intermediates, fungicides, heterocyclic ligands and others [5–8]. Early precedents for the oxidation of **1–2**, however, suffer from drawbacks such as the use of stoichiometric amount of relatively expensive oxidant (NaOCl, pyridinium chlorochromate *etc.*) and the over-oxidation of **2** to 2,5-furandicarboxylic acid (2,5-FDCA) [9]. Consequently, the use of O₂, or preferably air, as the oxidant has been studied intensively. Carlini *et al.* and Corma *et al.* reported the oxidation of **1–2** in air at high temperatures with vanadium-based heterogeneous catalysts (Scheme 1a and b) [10]. Xu *et al.* developed a bimetallic CuNO₃/VOSO₄ catalytic system that allows room temperature (RT) oxidation, albeit under O₂ [11]. Very recently, Riisager *et al.* discovered that such oxidation reactions can also be

achieved efficiently in air at 50 °C using CuCl/TEMPO/Bipy as the catalyst (Scheme 1d) [12]. In 2012, our group reported an environmentally benign catalyst K-OMS-2 for the oxidation of **1–2** in O₂ at 110 °C with excellent yield and selectivity (Scheme 1e) [13]. Other catalytic systems, such as Ru, Co, Mn and others [14–17], have also been developed for oxidation. Yet, the development of efficient catalysts for the oxidation of **1–2** in air remains an important challenge.

Herein, we disclose a new protocol using an iron catalyst that allows for the oxidation of **1–2** in air at room temperature. This study was inspired by the work of Ma and co-workers, in which an iron catalyst was developed for the oxidation of benzyl alcohols, allenols and propargylic alcohols to the corresponding aldehydes under O₂ [18]. The present study not only provides an alternative route for the synthesis of **2** from **1**, but also represents a rare example for the application of iron catalysts in the transformations of biomass.

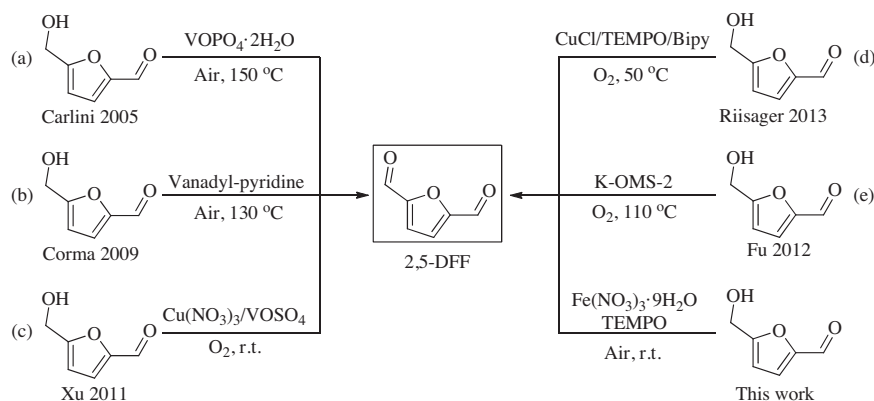
2. Experimental

2.1. General conditions

All reagents were used as received from commercial sources unless specified otherwise, or prepared as described in the literature. ¹H NMR, ¹³C NMR, spectra were recorded on a Bruker advance 400 spectrometer at ambient temperature in CDCl₃ unless otherwise noted. Data for ¹H NMR are reported as follows:

* Corresponding authors.

E-mail addresses: hjxu@hfut.edu.cn (H.-J. Xu), fuyao@ustc.edu.cn (Y. Fu).

**Scheme 1.** The processes for the oxidation of 5-HMF to 2,5-DFF.

chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C NMR are reported in chemical shifts (δ ppm). Gas chromatographic (GC) analyses were performed on a Shimadzu GC-2014 series GC system equipped with a flame-ionization detector using biphenyl as an internal standard. The temperature was 150 °C. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200–300 mesh).

2.2. The typical process for aerobic oxidation of 5-HMF to 2,5-DFF

5-HMF (63 mg, 0.5 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (10.1 mg, 0.025 mmol, 5 mol%), TEMPO (7.8 mg, 0.025 mmol, 5 mol%), NaCl (1.5 mg, 0.025 mol, 5 mol%) were charged into a tube, and then 2 mL of DCE was added. The reaction mixture was stirred at room temperature for 4 h in open air. Then, the reaction was monitored by GC analysis using 5-methyl-2-furaldehyde as an internal standard.

Separation of 2,5-DFF from reaction solution: after the epinephelos solution was filtered and washed with ethyl acetate for three times, the organic solvents were evaporated and the crude product was purified by flash column chromatography (PE:EA = 3:1) to give the desired product in 88% yield (detected by ^1H NMR). ^1H NMR (400 MHz, CDCl_3): δ 9.84 (s, 2H), 7.33 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 179.34, 154.30, 119.43.

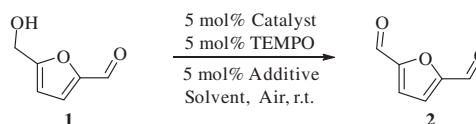
2.3. The synthesis of 2,5-FDCA

2,5-DFF (62 mg, 0.5 mmol) were charged into a tube, and 0.5 mL of *tert*-butyl hydroperoxide (TBHP, 70% in water) (7 equiv.) was added. The tube was stirred at 110 °C for 6 h. The liquid was evaporated under reduced pressure, and then washed by ethyl acetate for 3 times, the remaining solid was dried in high vacuum to afford 90% yield of 2,5-FDCA (detected by ^1H NMR). ^1H NMR ($\text{DMSO}-d_6$, 400 MHz): δ 7.29 (s, 2H), 13.67 (br. s, 2H). ^{13}C NMR ($\text{DMSO}-d_6$, 100 MHz): δ 118.84, 147.52, 159.40.

3. Results and discussion

Our results indicate that $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ /TEMPO can catalyze the oxidation of **1**–**2** in air at room temperature. The initial test was performed in dichloromethane (DCM), giving a 59% yield and a 99% selectivity (Table 1, entry 1). Control experiments revealed that the reaction shut down completely without the addition of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or TEMPO (Table 1, entries 2 and 3). Next, we examined a number of halide salts for the oxidation process. It was found that the use of NaBr, KCl and NaCl can improve significantly the yield of **2** from 59% to 68%, 78% and 80%, respectively (Table 1,

entries 4–6). NaF is the only exception, which slightly decreased the yield of **2** to 54% (Table 1, entry 7). Halide anions have been shown to act as ligands for transition metals [19]. The Cl^- from NaCl may act as a special electron-donating ligand to provide electrons to the d orbitals of Fe^{3+} to accelerate the semi-oxidative addition-type coupling with TEMPO (A proposed mechanism was shown in the Supporting information) [18]. Other metal catalysts such as $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, AgNO_3 , $\text{Pd}(\text{NO}_3)_2$ and FeCl_3 could also initiate the reaction, albeit giving lower yields of **2** (Table 1, entries 8–11). In general, the reaction yield can be further improved by using other organic solvents (Table 1, entries 12–17). However, when the reaction was conducted in water, only a trace amount of **2** could be obtained (Table 1, entry 18). The use of 1,2-dichloroethane (DCE) as the solvent gave the best result (GC yield, 92%; isolated yield, 88%) (Table 1, entry 16).

Table 1
Fe/TEMPO catalyzed oxidation of 5-HMF to 2,5-DFF in air at room temperature^a.

Entry	Additive	Catalyst	Solvent	Yield (%) ^b
1 ^c	–	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	DCM	59
2 ^d	–	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	DCM	Trace
3 ^e	–	/	DCM	Trace
4	NaBr	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	DCM	68
5	KCl	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	DCM	78
6	NaCl	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	DCM	80
7	NaF	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	DCM	54
8	NaCl	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	DCM	20
9	NaCl	AgNO_3	DCM	17
10	NaCl	$\text{Pd}(\text{NO}_3)_2$	DCM	37
11	NaCl	FeCl_3	DCM	32
12	NaCl	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	EtOAc	86
13	NaCl	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	THF	80
14	NaCl	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	CH_3CN	70
15	NaCl	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Dioxane	85
16 ^f	NaCl	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	DCE	92 (88) ^g
17	NaCl	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Toluene	84
18	NaCl	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	H_2O	trace

^a Reaction conditions: 5-HMF (0.5 mmol), additive (0.025 mmol, 5 mol%), TEMPO (0.025 mmol, 5 mol%), catalyst (0.025 mmol, 5 mol%), in solvent (2 mL), open to air at room temperature for 4 h.

^b GC yields were determined using 5-methyl furfural as an internal standard.

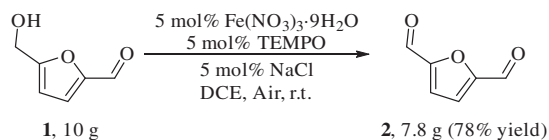
^c DCM = dichloromethane.

^d Without TEMPO.

^e Without $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

^f DCE = 1,2-dichloroethane.

^g Isolated yield in the parenthesis.



Scheme 2. Gram-scale synthesis of 2,5-DFF.

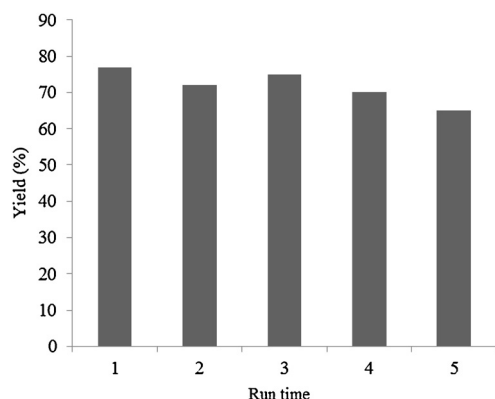
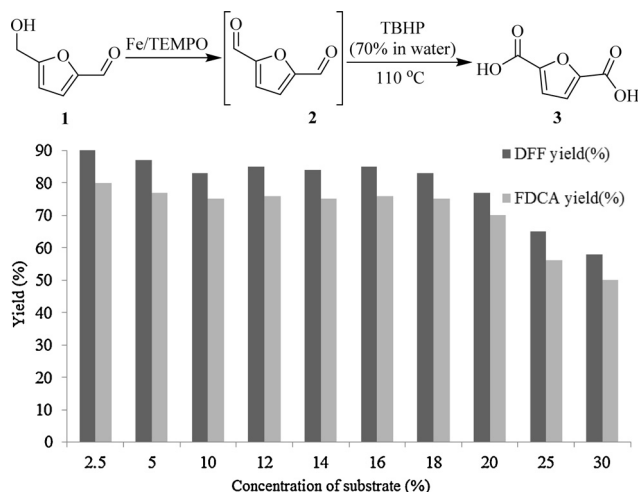


Fig. 1. The reusability of the catalyst system.

Remarkably, the optimized protocol is also efficient for a multigram-scale synthesis of **2**. As shown in Scheme 2, 10 g of **1** with 5 mol% $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, TEMPO, and NaCl in DCE at room temperature using air as the oxidant afforded 7.8 g of **2** in 10 h (recrystallized yield, 78%).

The recyclability of the catalyst further demonstrates the great potential of this new protocol in practical applications (Fig. 1). A simple distillation of a crude reaction product mixture led to an efficient recovery of the active catalyst. A 65% yield of **2** (recrystallized yield) was achieved even after recycling the catalyst for 4 times.

Finally, we developed a two-step process for the synthesis of 2,5-FDCA (**3**), an important derivative of 5-HMF [1a,4b], based on the new iron-catalyzed protocol. This process involves (1) the selective oxidation of **1**–**2**, (2) a simple oxidation of **2**–**3** by *tert*-butyl hydroperoxide (TBHP). Compound **3** has been identified as one of the twelve platform chemicals [20], which is useful for the synthesis of bio-degradable polymers [21,4a]. The direct synthesis of **3** from **1** has been achieved using stoichiometric oxidants (KMnO_4) or homogeneous catalysts (Co/MnBr) [15b]. Recently, a



Scheme 3. One-pot synthesis of 2,5-FDCA from HMF via 2,5-DFF.

number of heterogeneous catalytic systems for the synthesis of **3** have also been developed. However, these reported protocols only work at low substrate concentrations (typically <2 wt%) [22], limiting their practical applications. With our new process, moderate to good yields of **3** were achieved at significantly higher substrate concentrations (Scheme 3). For instance, an 80% yield of **3** was obtained when the substrate concentration of **1** was 2.5%. Even with a much higher concentration of **1** (18%), a 75% yield of **3** was obtained.

4. Conclusion

In conclusion, we identified an inexpensive, efficient, and selective iron catalyst for the oxidation of 5-HMF to 2,5-DFF in air at room temperature. The catalyst showed excellent recyclability for multigram-scale syntheses. Furthermore, a two-step process was developed successfully for the oxidation of 5-HMF to 2,5-FDCA at remarkably high substrate concentrations. Further studies to improve the catalytic system for the conversion of biomass to chemicals are currently undergoing.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ccllet.2015.07.001>.

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