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Fe_3O_4@SiO_2–TEMPO as a Magnetically Recyclable Catalyst for Highly Selective Aerobic Oxidation of 5-Hydroxymethylfurfural into 2,5-Diformylfuran under Metal- and Halogen-Free Conditions

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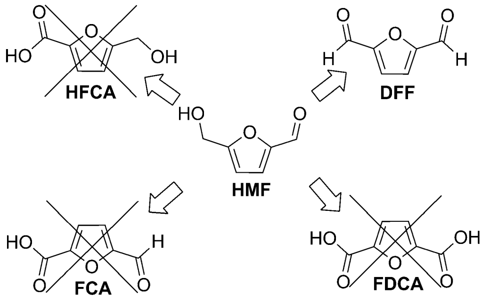
A highly selective aerobic oxidation of 5-hydroxymethylfurfural (5-HMF) into 2,5-diformylfuran (DFF) by employing a magnetically separable 2,2,6,6-tetramethylpiperidine-*N*-oxide (TEMPO) catalyst (Fe_3O_4@SiO_2–TEMPO) under metal- and halogen-free conditions is described. Quantitative yields of DFF with excellent selectivities as high as $>99\%$ were achieved under several versatile reaction conditions in a catalytic system consisting of Fe_3O_4@SiO_2–TEMPO as a catalyst, *tert*-butyl nitrite as a co-catalyst, acetic acid as an additive, and toluene as a solvent. The results clearly demonstrate that the present catalytic system for selective conversion of 5-HMF into DFF is comparable or even superior to the many systems based on transition-metal catalysts. In addition, the catalyst can be successfully recovered and reused in five consecutive reaction runs by an external magnetic source with keeping its catalytic performance and selectivity.

Over the last century, the world has concerned with crude-oil replacement with other sources of energy as a result of the depletion of fossil oil reservoirs and the awareness of climate change. In this regard, biomass is the most fascinating alternative feedstock, as it is the only widely attainable carbon source apart from oil and coal.[1] Production of fuels and chemicals from biomass can be typically achieved through partially deoxygenating biomass derivatives, which primarily is derived from hydrolysis and dehydration methods, to produce a variety of fuels, fuel additives, and fine chemicals.[2] For example, hexose monosaccharaides such as glucose and fructose and even polysaccharides such as cellulose are able to be catalytically dehydrated into 5-hydroxymethylfurfural (5-HMF), a versatile biobased platform chemical with high potential. In particular, it is well documented that the HMF itself is a key intermediate for the production of 2,5-furandicarboxylic acid (FDCA) thorough oxidation by employing various stoichiometric oxidizing agents and catalysts.[3] The US Department of Energy biomass program has identified FDCA as one of the twelve chemicals obtained from biomass in biorefineries that in turn can be replaced with petroleum-derived chemical building blocks such as terephthalic, isophthalic, and adipic acids, which are currently used in polymer technology.[4] 2,5-Diformylfuran (DFF), is another important platform derived from HMF that can be used, for example, as a starting material for the synthesis of the pharmaceuticals, macrocyclic ligands, and others.[5] Although DFF is recognized as a top value-added chemical obtainable from biomass, so far only limited attention has been paid to its synthesis.[6] DFF can be prepared through partially oxidation of the hydroxymethyl group in HMF, which behaves like primary alcohols bearing an aromatic moiety. Thus, DFF can be compared to a certain extent with benzyl or furfuryl alcohol (Scheme 1).[7] However, the main challenge of this important process is the existing both furan and aldehyde functionalities in HMF, which makes it susceptible to undergoing many side reactions such as overoxidation to FDCA and/or 5-formyl-2-furancarboxylic acid, decarbonylation, and cross-polymerization to produce unwanted byproducts.



Scheme 1. Selective oxidation of HMF into DFF rather than 2-hydroxymethylfurancarboxylic acid (HFCA), FCA, or FDCA.

As claimed by several relevant research works, oxidation of the hydroxyl group in HMF proceeds much slower than oxidation of the aldehyde moiety.[8] Therefore, the development of novel catalyst systems for efficient and selective oxidation of HMF into DFF is a great challenge. In this way, the concomitant use of molecular oxygen or air and heterogeneous oxidation catalysts, which can be reused in liquid phase reactions, is highly favored from both sustainable chemistry and economical point of views. To date, several metal-based catalytic systems such as Co/Mn/Zn/Br,[9] Pt–Bi/C,[10] various types of vana-

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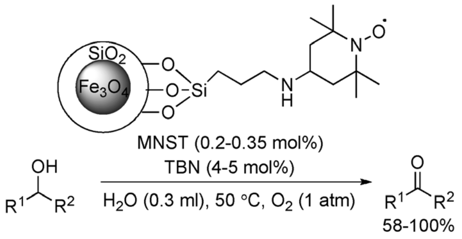
dium-based catalysts,[6,11] Ru/HT,[12] and $KMn_8O_{16}{\cdot}n\,H_2O$[13] have been utilized with varied degrees of success in the selective aerobic oxidation of HMF into DFF.

Several promising catalyst systems such as 2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO) in combination with stoichiometric halogen-based oxidants[14a] and/or halogen based solvent,[14b] and TEMPO/CuCl/O_2 either in the absence[14a] or in the presence[15] of nitrogen-containing promoters have also been employed for the same transformation. However, although the selectivity toward DFF and product yields was addressed in the above-mentioned pioneering efforts, there are several important issues that should be still resolved. One of the important drawbacks of current liquid-phase catalytic oxidation of HMF relate to the use of transition-metal catalysts or cocatalysts,[9–15] which are potentially difficult to separate from the products. In addition, many of the present protocols require high reaction temperatures (up to 150 °C),[9,12] and/or high oxygen pressure (up to 10 bar),[6,11] to ensure desirable DFF selectivities at high HMF conversions. Acknowledging these important achievements, the quest for milder and greener methodologies by designing metal-free catalyst systems for selective aerobic oxidation of HMF into DFF remains a great challenge. In this regard, the TEMPO radical seems to have an intriguing prospect in the field of metal-free aerobic oxidation of alcohols.[16] Along the line of this hypothesis and our continuous interest in developing novel systems for aerobic oxidation of alcohols,[17] we have recently introduced a new system based on magnetic silica-coated Fe_3O_4-nanoparticles-supported TEMPO (MNST) in the aerobic oxidation of varied alcohols under metal- and halogen-free conditions (Scheme 2). Considering the excellent catalytic performance of MNST in performing alcohol oxidation to aldehydes[18a] and one-pot oxidative three-component Passerini reaction,[19] we reasoned that this catalyst might be equally applicable for accomplishing the selective oxidation of HMF into DFF.



Scheme 2. MNST catalyst for aerobic oxidation of a variety of alcohols.

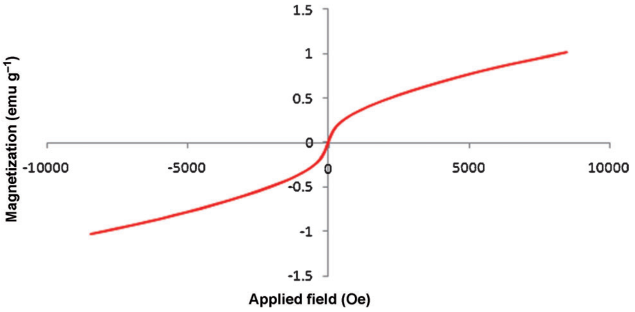


Figure 1. Vibrating sample magnetometer curve of MNST using KAVIR magnetometer.

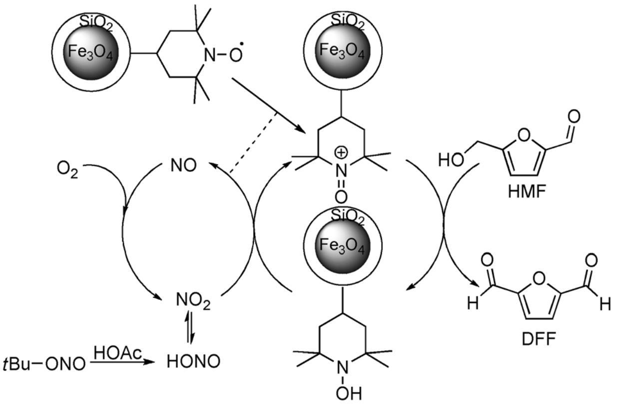
Table 1. Aerobic oxidation of HMF into DFF over MNST catalyst.

Entry	MNST[a] [mol %]	Solvent [mL]	T [°C]	Additive[b]	TBN [mol %]	t [h]	DFF yield[c] [%]
1	0.2	water (0.3)	50	–	5	24	18
2	0.2	water (0.3)	50	–	50	24	70
3	0.2	water (2)	50	–	50	24	15
4	0.2	water (2)	50	HOAc	5	24	30
5	0.2	water (2)	50	HOAc	50	24	38
6	0.2	HOAc (0.5)	RT	–	50	3	> 99
7	0.2	toluene (2)	RT	HOAc	50	2	> 99
8	0.2	toluene (2)	RT	HOAc	50	5	> 99
9	–	toluene (2)	RT	HOAc	50	24	7
10	0.2	toluene (2)	RT	HOAc	–	24	10
11	0.1	toluene (2)	RT	HOAc	50	10	> 99
12	0.1	toluene (2)	RT	HOAc	40	12	> 99
13	0.1	toluene (2)	RT	HOAc	30	18	> 99
14	0.1	toluene (2)	RT	HOAc	20	24	60
15	0.1	toluene (2)	RT	HOAc	10	24	40
16	0.5	toluene (2)	RT	HOAc	10	24	45
17	0.5	toluene (2)	50	HOAc	10	24	> 99
18	0.5	toluene (2)	RT	HOAc	20	24	> 99
19	1	toluene (2)	50	HOAc	10	12	> 99
20	1	toluene (2)	50	HOAc	5	24	70
21	2	toluene (2)	50	HOAc	5	18	> 99
22[d]	2	toluene (2)	50	HOAc	5	18	> 99
23[e]	2	toluene(10)	50	HOAc	5	18	> 99

[a] MNST loading ≈0.31 mmol g^{-1} according to CHN analysis. [b] (HOAc) 15 mg was added as an additive. [c] GC yield. [d] HMF 1 mmol was used. [e] 5 mmol HMF was used (the amount of solvent was not optimized).

Firstly, we aimed to prepare and re-characterize MNST by following our previous method.[18] The magnetic properties of MNST catalyst were investigated by using a vibrating sample magnetometer at room temperature by Meghnatis Daghigh Kavir Company (Iran). As illustrated in Figure 1, the magnetization curves of the prepared materials exhibited no hysteresis loop, which demonstrates its superparamagnetic characteristics. Also, N_2 sorption analysis at 77 K revealed a type (III) isotherm specifying a nonporous material, in which BET surface area calculation indicated a surface area of 50 $m^2\,g^{-1}$ (Supporting Information, Figure S9, S10). On the basis of the observation that MNST exhibited excellent catalytic activity under the conditions demonstrated in Scheme 2, we began our investigations on the aerobic oxidation of HMF using essentially the same reaction condition (Table 1, entry 1). To our surprise, the initial results in pure water (0.3 mL) were rather disappointing because DFF was obtained in poor yields of 18 % after 24 h. Although the yield of DFF was strongly improved upon employing large amounts of *tert*-butyl nitrite (TBN, up to 50 mol %), the results were not reproducible because of the difficulty of mixing the reaction mixture (entry 2).

In addition, the reaction did not reach completion even by using such these high loadings of TBN. To solve the mixing problem, the reaction was then performed by using a larger water volume of 2 mL under otherwise the same reaction conditions. However, the oxidation reaction of 5-HMF proved to be again unsatisfactory under these conditions (Table 1, entry 3). In an attempt to improve the catalyst performance, we examined the use of acetic acid as additive (entries 4 and 5), whereby we took into account our earlier findings[16u,20] of a strong favorable influence of HOAc on the catalytic activity of TEMPO in the aerobic oxidation of alcohols under metal-free conditions. The beneficial effect of HOAc was immediately realized, but the catalyst efficiency did not improve much because the yield of DFF hardly reached to 38% even after prolonged reaction times under these conditions. For further improving the catalyst performance, we next examined several reaction conditions by emphasizing the fact that the employment of lower amounts of TBN would be more favorable from the standpoint of both green and sustainable chemistry. We found that the DFF yield was dramatically increased to >99% within only 3 h if the reaction was conducted in pure HOAc as reaction solvent (entry 6). The same level of the yields and also DFF selectivities were also obtained in shorter reaction time of 2 h if toluene was employed in the presence of small quantities of HOAc (15 mg, entry 7). The reaction proceeded still well at room temperature and selectively delivered DFF in quantitative yields after somewhat longer reaction times (entry 8). Blank runs using either MNST (0.2 mol%) or TBN (50 mol%) alone gave no conversion, indicating the key importance of coexistence of these materials for driving the successful aerobic oxidation of 5-HMF (entries 9,10). In addition, by reducing the amount of MNST from 0.2 mol% to 0.1 mol%, the same excellent yields of DFF were still obtained in the presence of 50 mol% TBN at room temperature (entry 11). This system also reached completion in somewhat longer reaction times of the reaction (typically 12–18 h) in the presence of lower TBN loading (up to 30 mol%), but the yields of DFF were significantly reduced to 40% upon further decreasing the TBN loading to 10–20 mol% (entries 12–15). Although further increasing of MNST loading from 0.1 mol% to 0.5 mol% offered no advantages in the presence of 10 mol% TBN at room temperature, the same reaction system led to DFF with excellent conversion and selectivity at 50 °C (entries 16 and 17). Further studies revealed that the same high DFF yields and selectivities were also obtained by employing 20 mol% TBN, 0.5 mol% MNST at room temperature (entry 18). It was also found that a small increase in MNST loading to 1–2 mol% could significantly improve the efficiency of the reaction at >99% conversion and selectivity in the presence of as low as 5 mol% TBN (entries 19–21). Furthermore, to show the potential application of this catalytic system for large-scale operation, the oxidation of HMF was studied on either 1 or 5 mmol scale under the optimized conditions demonstrated in entry 21. Interestingly, no detectable change in DFF yield and selectivity was observed over MNST catalytic system compared to the case of the small-scale experiments (entries 22 and 23). On the basis of several relevant studies underlying the overall mechanism for metal-free aerobic oxidation of alcohols using homogeneous TEMPO in the presence of various NO_x sources,[16v–z] a possible reaction pathway was proposed and is depicted in Scheme 3, in which the mediation of electron transfer from alcohol to O_2 by NO/NO_2 couples and immobilized nitroxyl radical (MNST) through a combination of two redox cycles is highlighted.



Scheme 3. Proposed reaction pathway for the aerobic oxidation of HMF into DFF using MNST catalyst.

After oxidation of 5-HMF under the conditions obtained in Table 1 entry 22, MNST was quantitatively separated from the reaction mixture by employing an external magnetic field, thoroughly washed with ethanol, and reutilized in subsequent runs under identical reaction conditions. The results indicate that no efficiency loss was observed in 5-HMF oxidation in up to four successive runs (Figure 2).[21]

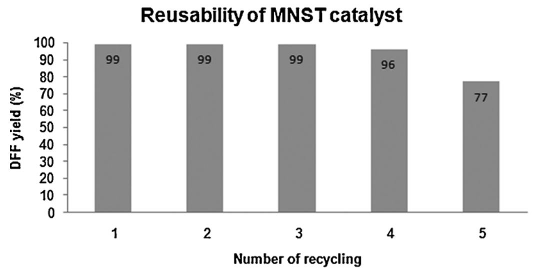


Figure 2. Reusability of MNST catalyst in the oxidation of HMF into DFF; HMF (1 mmol), MNST (2 mol%), toluene (2 mL), TBN (5 mol%), HOAc (75 mg), 50 °C, 18 h.

It was also noticed that the catalyst exhibited little (almost no) morphological changes as evidenced by comparison of TEM images before and after catalysis (Figure 3). The preferential formation of DFF with excellent selectivity in all reactions demonstrated in Table 1 and also during the recycling experiments is particularly noteworthy, because no detectable amounts of either FDCA or 5-formyl-2-furancarboxylic acid were observed in the products.

In conclusion, we have developed a new aerobic oxidation system for the selective oxidation of 5-hydroxymethylfurfural (5-HMF) into 2,5-diformylfuran (DFF) using a magnetically separable organocatalyst (Fe_3O_4@SiO_2–TEMPO, MNST). This reaction was performed under transition-metal- as well as halogen-free conditions, which is suitable from the viewpoint of green and sustainable chemistry. Notably, the superparamagnetic nature

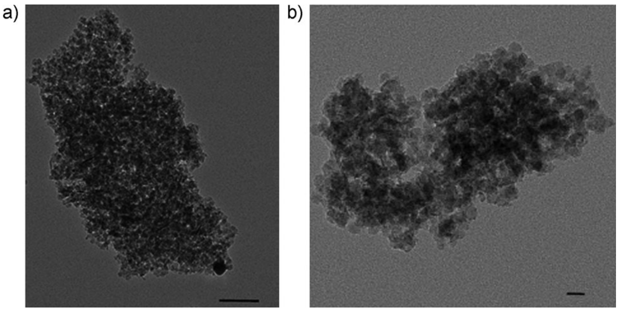


Figure 3. TEM micrographs of MNST a) before catalysis (scale bar 100 nm) and b) after five reaction cycles (scale bar: 20 nm) of the oxidation of HMF into DFF; HMF (1 mmol), MNST (2 mol %), toluene (2 mL), 5 mol % TBN, 75 mg HOAc, 50 °C, 18 h.

of the MNST catalyst facilitates easy separation of the catalyst from reaction media by simply employing an external magnetic field. The quantitative yields of DFF was achieved in excellent chemoselectivity (>99 %) under several versatile reaction conditions as demonstrated in Table 1. In this way, the catalyst can be successfully recovered and reused in five consecutive reaction runs, keeping its catalytic performance and selectivity. To our knowledge, this method is the first report on the selective aerobic oxidation of 5-HMF using magnetically separable catalysts under metal- as well as halogen-free conditions. It is believed that this finding will stimulate new areas in designing novel solid catalysts in a designated pathway with appropriate catalytic performance and recycling properties to control the selectivity of this important transformation, addressing economic and environmental issues.

Experimental Section

A typical catalytic procedure for 5-HMF oxidation to the desired 2,5-diformylfuran: In a 10 mL two-necked flask, 5-HMF (1 mmol), MNST (2 mol %), HOAc (75 mg), and toluene (2 mL) were charged. To this mixture, TBN (5 mol %) was added. Then the flask was evacuated and recharged with pure oxygen for three times and finally was charged with pure oxygen (balloon filled, $PO_2 \approx 1$ atmosphere). The resulting mixture was stirred (800 rpm) at 50 °C for 18 h. After this time, the catalyst was simply separated by employing an external magnetic field and the resulting solution was analyzed by GC for conversion and selectivity determination by using standard addition methods. Moreover, after completion of the aerobic oxidation and magnetic separation of the catalyst, the solvent was evaporated under reduced pressure and the remaining white solid was analyzed by NMR spectroscopy (see the Supporting Information).

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Keywords: alcohols · biomass · heterocycles · magnetic properties · oxidation

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[21] In a separate experiment, we have also employed the conditions described in entry 7 of Table 1 [HMF (0.2 mmol), TBN (50 mol %), MNST (0.2 mol %), toluene (2 mL), AcOH (15 mg), at RT] for the catalyst recycling. We noticed that at RT the catalyst can be recycled in 14 successive reaction cycles without any significant loss of catalytic activity giving consistently excellent yields of DFF (>99 %). Such an impressive stability of immobilized TEMPO is certainly owing to the fact that all recycling reactions proceeded at low reaction temperature (RT) and low reaction times (2 h). However, this recycling could be only attained at the expense of employing large amounts of TBN (50 mol %) in each run, which is not certainly attractive form a practical point of view.

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