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Catalytic Synthesis of 2,5-Furandicarboxylic Acid from Concentrated 2,5-Diformylfuran Mediated by N-hydroxyimides under Mild Conditions

Fei Xia,[a, b] Jiping Ma,*[b] Xiuquan Jia,[a] Meiling Guo,[c] Xuebin Liu,[c] Hong Ma,[a] Jin Gao,[a] Jie Xu*[a]

Abstract: Producing polyester monomer 2,5-furandicarboxylic acid (FDCA) from biomass as an alternative to fossil-derived terephthalic acid has drawn much attention from both academy and industry. In this work, an efficient FDCA synthesis was proposed from 10.6 wt% 2,5-diformylfuran (DFF) in acetic acid using a combined catalytic system of Co/Mn acetate and N-hydroxyimides. The intermediate product of 5-formyl-2-furandicarboxylic acid (FFCA) possesses the least reactive formyl group. NHSI (N-hydroxysuccinimide) was found to be superior to NHPI (N-hydroxyphthalimide) in catalyzing the oxidation of the formyl group in FFCA intermediate, affording a near 95% yield of FDCA under mild conditions of 100 °C. Trace maleic anhydride was detected as by-product, which mainly came from the oxidative cleavage of DFF via furfural, furoic acid and 5-acetoxyl-2(*5H*)-furanone as intermediates.

Introduction

Producing value-added chemicals from renewable biomass resources has received increasing academic and industrial attention.[1] 2,5-Furandicarboxylic acid (FDCA) has similar conjugated and isoelectronic structures as purified terephthalic acid (PTA), which makes it a promising alternative to PTA in the production of poly(ethylene furanoate) (PEF) as a furan counterpart to poly(ethylene terephthalate) (PET).[2] In addition, PEF were found to show superior properties to PET in barrier performance for O_2, H_2O vapor and CO_2 and thermal properties,[3] which stoked an increased excitement in the production of FDCA.

Currently, FDCA was mainly synthesized by the catalytic oxidation of 5-hydroxymethylfurfural (HMF), a versatile platform molecule obtained from fructose,[4] glucose,[5] or cellulose.[6] Noble metal catalysts, such as supported Pt,[7] Au[8] and Pd[9] have been widely applied for the catalytic oxidation of HMF to FDCA.[10] Addition of stoichiometric base or a basic support is usually essential to give high FDCA yields. The rarity of noble metal and environmental concern caused by base additives hindered their wide application. On the other hand, the MC catalyst which is widely used in the *p*-xylene oxidation has been reported for the oxidation of HMF in batch reactor.[3a,11] With the promotion of acid or Zr additives, ca. 60% yield of FDCA were obtained.[12] However, HMF oxidation in these cases were either conducted in dilute solutions (usually lower than 2.1 wt.% in noble metal catalysis system) or only moderate yield FDCA can be obtained. This might be due to overactive hydroxymethyl and formyl group in HMF which might result in side-reactions to humins at high concentration during oxidation.

To solve the above-mentioned problems, reactive functional group protection strategies have been applied to suppress humins formation via etherification of hydroxymethyl[13] or acetalization of aldehyde group,[14] during the oxidation. Inspired by these work, 2,5-diformylfuran (DFF) could be used as feedstock instead of HMF to produce FDCA. DFF can be obtained via selective conversion of HMF or fructose.[15] It has simplified functional groups, thus the formation of monoacid 5-hydroxymethylfuran-2-carboxylic acid (HMFCA) and other possible side-reactions can be avoided. Moreover, high purity DFF production from HMF has been realized by our group in kilogram scale.[15a,b] Unlike the Co/Mn/Br system which is corrosive to equipment, organic free radical precursors such as N-hydroxyphthalimide (NHPI) and its analogues were previously used as an efficient alternative for the oxidation of hydrocarbon.[16] Herein, based on our previous work, we propose an efficient FDCA synthesis route through catalytic aerobic oxidation of concentrated DFF in acetic acid. The aldehyde groups both in DFF and the reaction intermediates were efficiently oxidized to corresponding acids, and about 95% yield of FDCA was obtained using the catalytic system of Co/Mn/N-hydroxysuccinimide under mild conditions.

Results and Discussion

Comparison of oxidation of DFF and HMF

Controlled experiments were initially carried out under the selected probe catalytic system of Co/Mn/NHPI using DFF and HMF as substrate in different concentration, respectively (Figure 1). Despite that both DFF and HMF were nearly completely converted at both 1.1 and 10.6 wt% concentration, moderate yield of FDCA (61.3 and 63.2%) was obtained in the oxidation of DFF and HMF at 1.1 wt% concentration. Besides, 26.0 and 12.1% yield of FFCA was detected respectively. However, when DFF and HMF were treated at 10.6 wt% concentration, only 34.9% yield of FDCA was observed through the oxidation of HMF, which is much lower than that obtained from DFF (90.6%). In addition, only 52.6% carbon yield was obtained from HMF oxidation at high concentration which is much lower than that obtained from DFF oxidation (98.6% carbon yield), suggesting that certain side-reaction occurs during the oxidation of concentrated HMF. In short, poor FDCA yield and carbon

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balance were observed during concentrated HMF oxidation, indicating that DFF was superior to HMF for the production of FDCA.

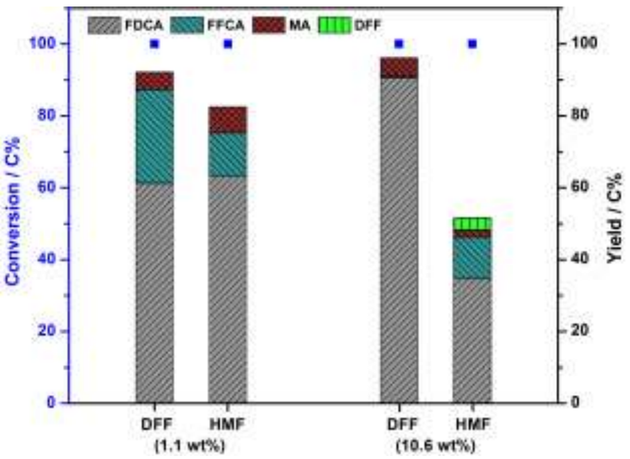


Figure 1. Product distribution of DFF oxidation and HMF oxidation. Reaction conditions: DFF or HMF (1 and 10 mmol), 5 mol% $Co(OAc)_2{\cdot}4H_2O$, 5 mol% $Mn(OAc)_2{\cdot}4H_2O$, 20 mol% NHPI, 10 mL HOAc, 140 °C, 1.0 MPa O_2, 110 min.

Oxidation of DFF to FDCA with O_2

DFF oxidation was studied under the probe catalytic system of Co/Mn/NHPI at 80 °C to screen the promoters (Co, or Mn, or Co/Mn) and N-hydroxyimides. It was found that DFF conversion was inefficient and almost no FDCA was detected when individually catalyzed by Co, Mn acetates and NHPI or by the combination of Co and Mn acetates (Table 1, entries 1-4). When NHPI was combined with Co or Mn acetates, DFF conversion increased dramatically to about 70%, and more than 20% of FDCA was obtained (Table 1, entries 5, 6). DFF conversion and FDCA yield were further improved when combined these three species. A 38.3% yield of FDCA with 30.7% yield of FFCA and 3.5% yield of MA were gained at the DFF conversion of 76.0% using the combination catalytic system of Co/Mn/NHPI, and the carbon balance was up to 98.2% (Table 1, entry 7). It is possible that with the assistant of Co/Mn acetate, NHPI can be efficiently transformed to phthalimide N-oxyl radical (PINO) to initiate the conversion of DFF to FDCA. The interaction between Co/Mn acetate and NHPI could be proposed as illustrated in the MC

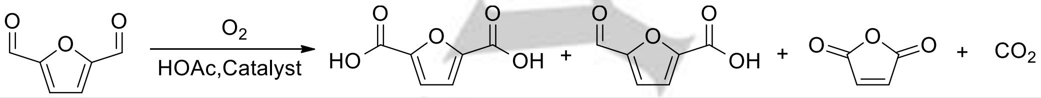


Table 1. Catalytic oxidation of DFF to FDCA with O_2.[a]

Entry	Catalyst (mol%)			Conv. (C%)	Yield (C%)				Carbon balance (C%)
	Co	Mn	NHPI		FDCA	FFCA	MA	CO_2[b]	
1	5	-	-	13.8	-	-	-	-	86.2
2	-	5	-	12.7	-	3.2	-	-	90.5
3	-	-	20	28.3	-	9.9	1.3	0.6	83.5
4	5	5	-	12.1	-	-	-	-	87.9
5	5	-	20	68.4	22.2	18.1	2.2	1.1	75.2
6	-	5	20	74.2	27.5	15.7	2.4	1.2	72.6
7	5	5	20	76.0	38.3	30.7	3.5	1.7	98.2
8[c]	5	5	20	> 99	90.6	0.4	5.1	2.5	98.6
9[c]	15	15	30	> 99	98.7	0.9	0.3	0.1	> 99

[a] Reaction conditions: 10 mmol DFF, $Co(OAc)_2{\cdot}4H_2O$, $Mn(OAc)_2{\cdot}4H_2O$, NHPI, 10 mL HOAc, 0.6 MPa O_2, 80 °C, 80 min. [b] The yield of CO_2 was evaluated according to the yield of MA. [c] Reaction conditions: 1.0 MPa O_2, 140 °C, 110 min.

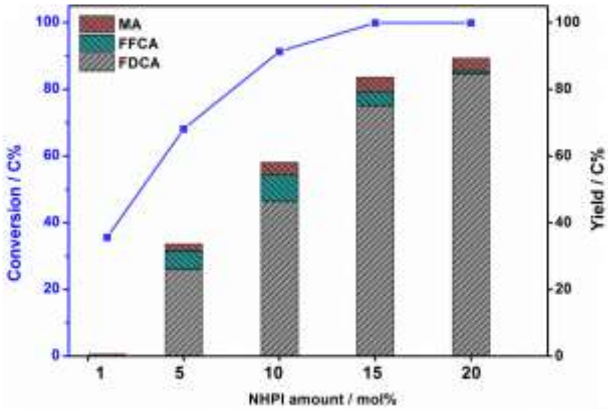


Figure 2. The influence of the NHPI dosage on DFF oxidation. Reaction conditions: 10 mmol DFF, 5 mol% $Co(OAc)_2·4H_2O$, 5 mol% $Mn(OAc)_2·4H_2O$, NHPI, 10 mL HOAc, 140 °C, 1.0 MPa O_2, 110 min.

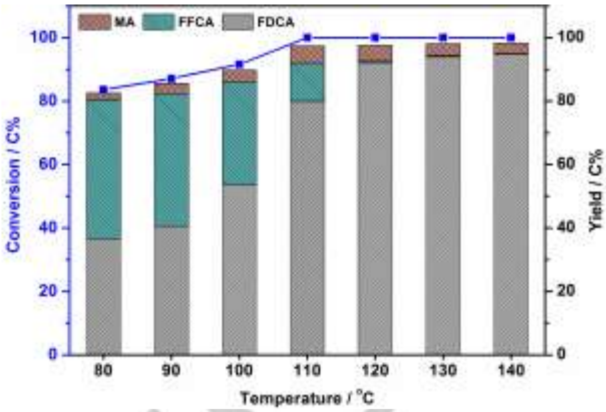


Figure 3. Temperature effects on DFF oxidation. Reaction conditions: 1 mmol DFF, 15 mol% $Co(OAc)_2·4H_2O$, 15 mol% $Mn(OAc)_2·4H_2O$, 30 mol% NHPI, 5 mL HOAc, 1.0 MPa air, 80 min.

catalysis system (Scheme S1).[12a,17] When the reaction temperature increased to 140 °C, a 90.6% yield of FDCA was obtained (Table 1, entry 8). Moreover, the influence of the NHPI dosage on the catalytic performance was further investigated. As seen in Figure 2, the conversion of DFF was positive correlation to the amount of NHPI. And the FDCA yield increased with the increase of the amount of NHPI. At the temperature of 140 °C, further modulation the molar ratio of Co, Mn and NHPI resulted in 98.7% yield of FDCA (Table 1, entry 9). These results demonstrated that the yield of FDCA should mainly depend on the composition of catalysts and reaction temperature. It is worth noting that trace amount of MA was detected in the presence of NHPI (Table 1, entries 3, 5-9).

Air as oxidant instead of pure oxygen

In our reaction, using pure oxygen as the oxidant may cause safety hazard. In order to decrease the experiments risk to a minimum, air was used instead of pure oxygen. Under identical oxygen partial pressure, the performance of air was comparable to that of pure O_2 (Table 2, entries 1-2). These results suggested that air could be used as an alternative to O_2 for our reaction.

Effect of temperature on DFF aerobic oxidation over NHPI

Table 2. Catalytic oxidation of DFF under the same partial pressure of O_2.[a]

Entry	Pressure (Oxidant) (MPa)	Conv. (C%)	Yield (C%)		
			FDCA	FFCA	MA
1	0.2 (O_2)	> 99	98.1	0.1	1.2
2	1.0 (air)	> 99	97.1	0.4	1.7

[a] Reaction conditions: 2 mmol DFF, 15 mol% $Co(OAc)_2·4H_2O$, 15 mol% $Mn(OAc)_2·4H_2O$, 30 mol% NHPI, 5 mL HOAc, 140 °C, 110 min.

As above-mentioned, 20-30 mol% NHPI relative to DFF was necessary to gain better FDCA yield. The major reason is that NHPI is unstable at higher reaction temperature. It would degrade to phthalic anhydride and phthalic acid.[16a] In other case, dimerization would occur when NHPI was converted to PINO.[18] Considering the instability of NHPI at higher temperature, the catalytic performance of NHPI at lower temperature was then explored. DFF oxidation was carried out at temperature range from 80 to 140 °C (Figure 3). When the temperature decreased to 120 °C, the results were similar to that of at 140 °C. For the tested temperature from 120 to 80 °C, the temperature plays a great role on the product distribution. When the temperature was decreased to 80 °C, the conversion of DFF decreased to 83.6%, the yields of FDCA decreased remarkably to 36.6%, and the major product was FFCA with a 43.9% yield. This implied that the conversion of intermediate FFCA was inefficient at lower temperature within 80 min.

Oxidation of DFF promoted by different N-hydroxyimides

Given that the catalytic performance of NHPI is inefficient at low temperature and the instability of NHPI during the oxidation, it's necessary to explore other organic free radical catalysts that

Table 3. Oxidation of DFF promoted by different N-hydroxyimides.[a]

Entry	N-hydroxyimides	Conv. (C%)	Yield (C%)		
			FDCA	FFCA	MA
1	NHSI	> 99	94.8	1.8	2.3
2	NHPI	91.6	51.9	31.4	3.6

[a] Reaction conditions: 1 mmol DFF, 15 mol% $Co(OAc)_2·4H_2O$, 15 mol% $Mn(OAc)_2·4H_2O$, 30 mol% N-hydroxyimides, 5 mL HOAc, 1.0 MPa air, 80 min, 100 °C.

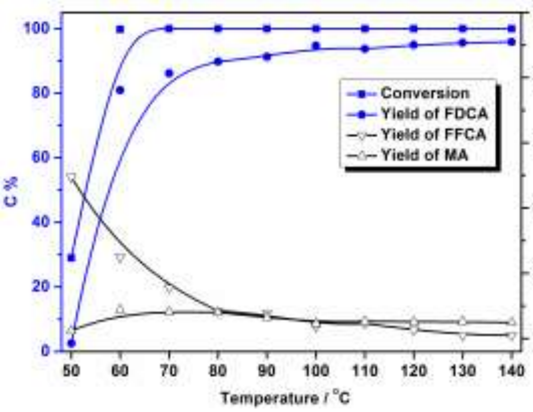


Figure 4. Temperature effects on DFF oxidation over NHSI. Reaction conditions: 1 mmol DFF, 15 mol% $Co(OAc)_2·4H_2O$, 15 mol% $Mn(OAc)_2·4H_2O$, 30 mol% NHSI, 5 mL HOAc, 1.0 MPa air, 80 min.

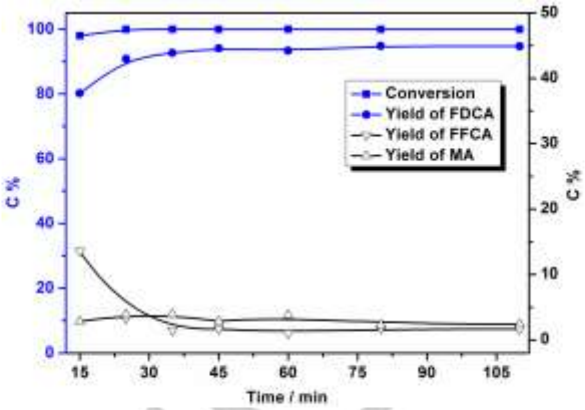


Figure 5. Time course of oxidation of DFF catalyzed by NHSI. Reaction conditions: 1 mmol DFF, 15 mol% $Co(OAc)_2·4H_2O$, 15 mol% $Mn(OAc)_2·4H_2O$, 30 mol% NHSI, 5 mL HOAc, 1.0 MPa air, 100 °C.

could treat the oxidation at lower temperature with relatively higher catalytic activity. N-hydroxysuccinimide (NHSI) is a novel radical precursor that is synthesized from succinic anhydride.[19] It has been reported that the N-hydroxyimides with larger O-H bond dissociation energies (BDEs) showed higher H-atom abstraction ability.[18c,20] Therefore, it would be expected that NHPI analogues with larger O-H BDEs would be more efficient for FDCA synthesis under mild conditions. According to the calculation results of Chen et al.[20d] the BDEs of NHSI is higher than that of NHPI (86.7 vs. 83.4 kcal/mol), In addition, the higher solubility of NHSI in acetic acid compared with NHPI (Figure S1) could contribute to better performance in catalytic reactions. The DFF oxidation was conducted under the catalysis of NHSI and NHPI respectively in the presence of Co/Mn at lower temperature of 100 °C. And the detailed results were listed in Table 3. As expected, DFF was fully converted in the presence of NHSI, whereas 91.6% conversion of DFF was observed when NHPI was used. The yield of FDCA follows the order as NHSI>NHPI, while the trend of FFCA yield was contrary.

Effect of temperature on DFF oxidation mediated by NHSI

Since NHSI shows higher activity than NHPI, it's necessary to study the catalytic performance of NHSI in detail. The temperature effect of NHSI on aerobic oxidation of DFF was studied from 50 to 140 °C (Figure 4). Remarkably, DFF was almost completely converted at 60 °C affording FDCA in more than 80% yield and FFCA as the intermediate product. The further conversion of FFCA was observed with increasing the temperature. At 100 °C, The FDCA yield was up to the peak and the FFCA yield was 1.8%. When temperature was elevated higher than 100 °C, there was no obvious change in the yield of FDCA and FFCA. There was tiny change in MA yield during the tested temperature range.

Time course of DFF oxidation over NHSI

To get more detailed information about the conversion of DFF and intermediate FFCA catalyzed by NHSI at 100 °C, time course was studied (Figure 5). Temperature reached 100 °C spending about 15 min, during which 98.0% of DFF was converted. Full conversion of DFF reached at 25 min. Meanwhile, the intermediate FFCA was gradually converted to FDCA leading to the yield of FDCA increased rapidly to 90.8%. After that the yield of FDCA was up to the peak in 45 min. Besides, MA was detected at the beginning of the reaction, and its variation was inconspicuous.

Formation route of MA

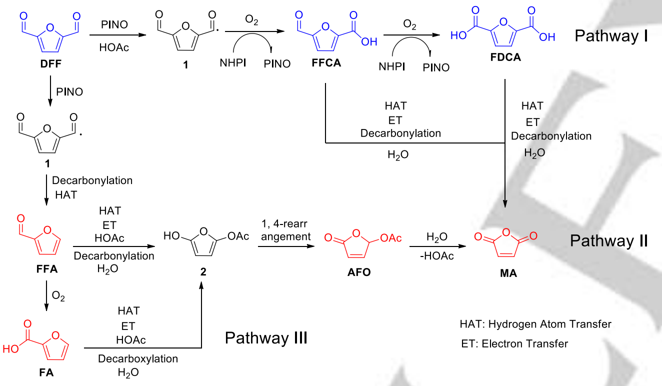
It's worth noting that the formation of MA was observed at the beginning of the reaction. In order to explore the formation route of the oxidative cleavage product MA, the oxidation of different substrates including DFF, FFCA and FDCA were tested under the selected probe catalytic system of NHPI (Table S1). A 2.8% yield of MA was gained in the oxidation of DFF. Under the same reaction conditions, the yields of MA were 1.0% and 0.6% for oxidation of FFCA and FDCA, respectively. These results implied that the formation of MA was a competing reaction and it mainly came from DFF.

It was reported that MA can be obtained from the oxidative cleavage of HMF,[21] and its formation route was proposed by Yin et al..[21b,22] In order to understand how MA was occurred in our reaction catalytic system, the possible intermediates were detected by GC-MS at the initial period. Trace amount of furfural (FFA) was detected at 10 min (Figure S2). In addition, CO_2 was detected by clear limewater and mass spectrometry (Figure S3 and S4). Thus it can be speculated that FFA was formed via decarbonylation of DFF, during which CO was oxidized to CO_2. In addition, as illuminated in the MC process, CO_2 could be derived from the oxidation of solvent HOAc.[23] As the reaction progress, trace amount of furoic acid (FA) was detected at 26 min (Figure S5). To identify whether FFA and FA were the intermediates for the formation of MA, control experiments were carried out using FFA and FA as the feedstocks, respectively. MA, FA and 5-acetoxyl-2(*5H*)-furanone (AFO) were detected during the oxidation of FFA at 10 min (Figure S6). In the case of FA oxidation, MA and AFO were also detected at the initial period (Figure S7). According to the above-mentioned results, a proposed route for MA formation (pathway **II** and **III**) was put forward in Scheme 1.

Reaction pathway

The proposed oxidation route of DFF under the tested catalytic system of NHPI was showed in Scheme 1. As to the oxidation of DFF to FDCA, the reaction may proceeds via pathway **I**, the hydrogen atom of aldehyde group is abstracted by PINO to generate the radical **1**, which might be oxidized by oxygen to give FFCA through peroxide radical and hydrogen peroxide intermediates. Then FFCA is oxidized to FDCA via similar steps.

On the other hand, the radical **1** may undergo decarbonylation and hydrogen atom transfer (HAT) to form FFA at the initial period. According to the intermediate AFO detected in GC-MS, AFO might form through 1,4-rearrangement of intermediate **2**,[22] which might generate from FFA via HAT, electron transfer (ET), HOAc attack on furan ring, and decarbonylation as well as reaction with H_2O. After HAT and ET, and reaction with H_2O, the major side-product of MA was formed after release of HOAc via pathway **II**. Besides, with the reaction proceeding, FA was formed via FFA oxidation. Meanwhile, FA may proceed with those similar steps such as HAT, ET, attacked by HOAc and decarboxylation as well as H_2O attack to generate intermediate **2** via pathway **III**. The following steps were similar as pathway **II**, with both AFO and MA were detected.



Scheme 1. Proposed oxidation route of DFF

Conclusions

In summary, an efficient FDCA synthesis through catalytic aerobic oxidation of concentrated DFF over Co/Mn acetate and N-hydroxyimides was reported. The intermediate product of FFCA was found to possess the less reactive formyl group in comparison with DFF. N-hydroxysuccinimide was much more active than N-hydroxyphthalimide in catalyzing the oxidation of the formyl group in FFCA intermediate at low temperature. About 95% yield of FDCA was obtained catalyzed by NHSI under mild conditions of 100 °C. Trace by-product of maleic anhydride was detected which mainly came from the oxidative cleavage of DFF. This work revealed that non-noble catalytic system is up to work for the efficient synthesis of FDCA from DFF under mild conditions.

Experimental Section

$Co(OAc)_2{\cdot}4H_2O$, $Mn(OAc)_2{\cdot}4H_2O$, furfural, glacial acetic acid were purchased from Sinopharm. NHPI (98%), NHSI (98%), FFCA (98%), FDCA (98%), furoic acid and maleic anhydride were supplied by Aladdin. DFF was prepared according to the previous report.[15a] Reagents were of analytical reagent grade and used without further purification unless otherwise stated.

The oxidation of DFF was performed in a 45 mL teflon-lined stainless steel autoclaves equipped with magnetic stirrer, pressure gauge and automatic temperature control apparatus. The reactor was connected to an oxygen/air cylinder for reaction pressure. In a typical experiment, DFF (1 mmol), $Co(OAc)_2{\cdot}4H_2O$ (0.15 mmol), $Mn(OAc)_2{\cdot}4H_2O$ (0.15 mmol), NHPI (0.30 mmol) and HOAc (5 mL) were loaded into the reactor. After sealing and charging with oxygen or air, the autoclave was heated to the desired temperature and kept for the desired reaction time under stirring. After the reaction, the autoclave was cooled down to room temperature. The residual gas was released carefully and collected for subsequent analysis.

The products were identified by Agilent 6890N GC/5973 MS as well as by comparison with the retention times to corresponding standards in gas chromatography (GC) and high performance liquid chromatography (HPLC) traces. The conversion of DFF and yield of MA were determined using a GC (Agilent 7890A) equipped with a FID detector and HP-5 capillary column (30 m × 0.53 mm × 1.5 μm). Mesitylene was used as the internal standard. After the GC sample was recovered, all the residuals were diluted to 100 mL using deionized water. The yields of FDCA and FFCA were analyzed with by HPLC (Waters e2695) with a column X Bridge C18 (4.6 mm × 150 mm, 5 μm) with UV detector. Methanol and 0.1 wt% phosphoric acid aqueous solution were used as the mobile phase, and the flow rate was 0.45 $mL{\cdot}min^{-1}$. Benzamide was used as the internal standard.

Acknowledgements

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Keywords: Catalytic oxidation • Biomass • Aldehyde • Carboxylic acid • N-Hydroxyimides

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Entry for the Table of Contents

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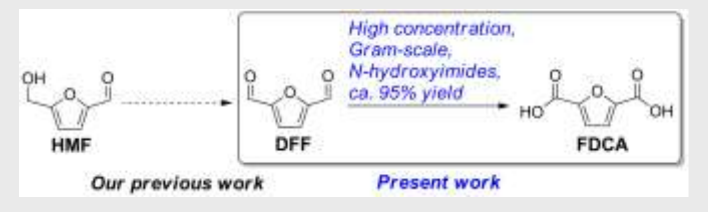

An efficient 2,5-furandicarboxylic acid synthesis route from aerobic oxidation of concentrated 2,5-diformylfuran mediated by N-hydroxyimides was described under mild conditions.

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Page No. – Page No.

Catalytic Synthesis of 2,5-Furandicarboxylic Acid from Concentrated 2,5-Diformylfuran Mediated by N-hydroxyimides under Mild Conditions