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Direct Synthesis of 2,5-Diformyfuran from Fructose with Graphene Oxide as Bifunctional and Metal-free Catalyst

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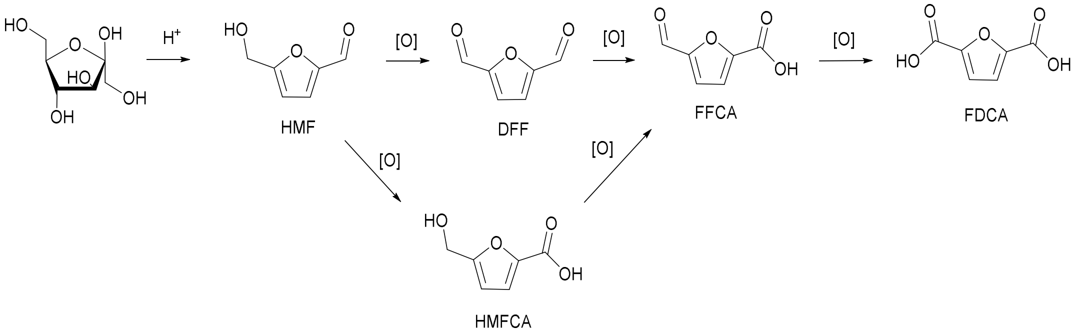
Abstract

Direct synthesis of 2,5-diformyfuran (DFF) from fructose is a tandem reaction that typically involves two steps catalyzed by two different catalysts, including fructose dehydration to 5-hydroxymethylfurfural (HMF) catalyzed by an acid catalyst and subsequent HMF oxidation to DFF catalyzed by a redox catalyst. In this study, graphene oxide, a metal-free carbon based material, was demonstrated to be an efficient and recyclable bifunctional catalyst in the direct synthesis of DFF from fructose. A DFF yield of 53.0% was achieved in a one pot and one-step (O_2, 24 h) reaction and the DFF yield could be further increased to 72.5% in a one pot and two-step reaction (N_2, 2 h and O_2 22 h).

1. Introduction

Rapidly depleting fossil fuels and escalating energy consumption coupled with rising environmental awareness among nations have led to an increased focus on the alternate, viable, ecofriendly, and renewable energy sources.[1] Based on this background, a growing interest has recently been devoted to fuels and chemicals from the sustainable biomass resource.[2-6]

5-Hydroxymethylfurfural (HMF), which is a dehydration product of C6-based carbohydrates, has been regarded as one of the most promising platform chemicals and can be used as a versatile precursor for the production of fine chemicals, plastics, pharmaceuticals and liquid fuels.[1] Selective oxidation of HMF is one of the most pivotal functional group transformations in the biorefinery.[7] The oxidation of HMF can generate several kinds of oxidation products such as 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), 5-formyl-2-furancarboxylic acid (FFCA), and 2,5-furandicarboxylic acid (FDCA), as depicted in Scheme 1. 2,5-diformylfuran (DFF), as an oxidation product of HMF, can be used for the synthesis of furan-containing polymers and materials with special properties. It can also be used as a starting material for the synthesis of various poly-Schiff bases, pharmaceuticals, antifungal agents, organic conductors and cross-linking agents of poly(vinyl alcohol) for battery applications.[8]



Scheme 1. Oxidation products of HMF derived from fructose dehydration.

DFF has primarily been synthesized from the oxidation of HMF by use of stoichiometric oxidants, including NaOCl,[9] $BaMnO_4$ [10]and pyridinium chlorochromate,[11] which not only requires stoichiometric oxidant but also produces large amounts of waste. In recent years, there is growing attention on the synthesis of DFF from the oxidation of HMF with molecular oxygen as the terminal oxidant by using heterogeneous or homogeneous metal-based catalysts like Co/Ce/Ru,[1] Ru,[1, 12, 13]Cu,[14] Cu/V,[15] Mn,[16] Mo/V,[17] V.[18, 19] The metal-containing catalysts often give a relative high DFF yield. However, the transition–metal–based catalysts applied in oxidation transformations are usually expensive, toxic and contaminative.[20]

On another side, HMF, currently obtained from the acid-promoted dehydration of fructose, is an expensive raw material for this purpose owing to its high cost in isolation and purification.[6] The progress in green chemistry could realize an integrated chemical process in which multistep reactions are consolidated in a one pot. Accordingly, the direct transformation of fructose to DFF in a one-pot process has recently attracted much attention and a series of combined catalyst system, such as H-form cation-exchange resin and $VOHPO_4$,[21] Amberlyst-15 and Ru/HT,[4] Fe_3O_4-SBA-SO_3H and K-OMS-2,[6] have been investigated as potential routes for DFF production from an economic and environmental point of view. In these combined catalytic systems, a mixture of an acid and a redox catalyst is essential for DFF production from fructose in a one pot and two-step approach. Under optimal conditions, the overall DFF yields from 45% [4, 21]to 80% [6] calculated on fructose were obtained by stepwise addition of these dual catalysts. Very recently, a one-pot as well as one-step approach to DFF with the yield of 60%,[17] 69.3%,[22] 84%,[23] 45%[24] was achieved respectively by using Mo or Mo-V containing Keggin heteropolyacid,[17, 22, 23] and proton- and vanadium- containing graphitic carbon nitride (V-g-$C_3N_4(H^+)$) [24] as bifunctional catalysts. The one-pot and one-step approach to DFF with bifunctional catalysts make it possible for producing DFF from fructose efficiently and economically.

Graphene oxide (GO), a readily available and inexpensive metal-free carbon material, historically, has functioned primarily as a precursor to reduced graphene oxide (rGO) or chemically modified graphene (CMG) materials.[25, 26] GO related materials have generated tremendous excitements owing to their remarkable electronic, mechanical and chemical properities.[27-31] The relatively harsh conditions used in GO typical synthetic protocols (Hummers method) introduced a variety of oxygen-containing functionalities (e.g. hydroxyl, epoxide, carboxylic acids, ketones, phenols, lactols and lactones).[32] As a result, these functionalities endow GO slightly acidic (pH 4.5 at 0.1 mg mL^{-1}) and rather strong oxidizing properties.[33] In the field of catalytic organic synthesis, GO has been applied extensively as an acid catalyst [34-37]or redox catalyst solely.[20, 33, 38-41] In GO material, the sulfonic groups and oxygen-containing groups show synergic effect in catalyzed fructose dehydration reaction [34] and the carboxylic acid groups, combined the unpaired electrons at the edge defects, show effective and selective dehydrogenation catalytic performance in alcohols [20]and amines.[38] Inspired by the acid and redox catalytic properties of GO material, here, we report the direct synthesis of DFF from fructose via reactions of an acid catalyzed dehydration and an successively aerobic oxidation with GO as a bifunctional and metal-free catalyst in a one-pot process. Up to 53.0% and 72.5% DFF yields were obtained in the one-pot, one-step and one-pot, two-step reactions, respectively.

2. Results and Discussion

2.1 Catalytic Aerobic Oxidation of HMF to DFF over GO.

The details of GO synthesis and characterization are described in Supporting information, and Figure S1-S2. It has been demonstrated that DMSO has obvious effect on suppressing undesired side reactions,[42] such as the degradation of HMF in the presence of acid catalyst and the formation of humus.[34, 43] In related repots, it is reported that the in situ thermolysis of DMSO at high temperature can generate strong acids such as sulfuric and methanesulfonic acids that could show catalytic ability at some extent in fructose dehydration.[44] Besides, it is suspected that the in situ formation of acids by thermolysis of DMSO at high temperature could act as catalysts in HMF oxidation.[44] Considering these results, DMSO was selected as the reaction solvent to illustrate the potential of GO material as the bifunctional catalyst in the one-pot synthesis of DFF from fructose.

Table 1. Aerobic Oxidation of HMF to DFF [a]

Entry	Catalyst	Catalyst Loading (mg)	T (°C)	t (h)	C_{HMF}	Y_{DFF}	Y_{FFCA}	$C_{balance}$
1	GO	20	120	24	< 5	< 3	0	---
2	----	---	140	24	37.5	26.9	7.51	96.9
3	GO	5	140	24	68.7	58.0	6.9	96.2
4	GO	10	140	24	83.4	70.6	7.8	94.6
5	GO	15	140	24	92.5	78.6	9.2	95.3
6	GO	20	140	24	100	90.0	7.6	97.6
7 [b]	----	----	140	24	45.7	0	0	54.3
8 [b]	GO	20	140	24	94.2	44.7	40.5	91.0

9 [c]	$KMnO_4$	0.02	140	24	39.0	27.2	7.20	95.4
10 [d]	1-pyrene carboxylic acid	30	140	24	79.3	58.6	15.4	93.3
11 [d e]	1-pyrene carboxylic acid	30	140	24	< 2	0	0	---
12 [e]	GO	20	140	24	< 2	0	0	----
13	GO	20	160	9	100	78.1	17.5	95.6

[a] Reaction condition: HMF, 2 mmol; DMSO, 4 mL; O_2, 20 mL min^{-1}.

[b] DMF was used as the reaction solvent instead of DMSO.

[c] 0.02 mg $KMnO_4$ was added into 4 mL DMSO as the catalyst.

[d] 30 mg 1-pyrene carboxylic acid was used as the catalyst in reaction.

[e] N_2, 20 mL min^{-1}.

Table 1 lists the results of DFF production *via* aerobic oxidation of HMF under different reaction conditions. As reported in our previous report,[41] the carboxylic acid groups in thermal exfoliated GO show high efficiency in catalytic oxidation of HMF to DFF with 2,2,6,6,-tetramethylpiperidin-1-oxyl (TEMPO) as the cocatalyst under relative mild conditions. However, the use of homogeneous TEMPO makes it difficult to recycle and high loading of GO material is needed to ensure the high HMF conversion.

In this work, the ultrasonic exfoliated GO, which contains abundant oxygen groups, was used as the bifunctional catalyst at relative high temperatures. In a preliminary experiment, 2 mmol HMF dissolved in 4 mL DMSO was heated to 120 ^{o}C in the presence of 20 mg GO for 24 h under an oxygen flow rate 20 mL min^{-1}, subsequent analysis showed that less than 5% HMF conversion was observed (Table 1, entry 1). After the reaction temperature increased to 140 ^{o}C, in the absence of GO, it was observed that the HMF conversion increased to 37.5 % with DFF yield to 26.9% (Table 1, entry 2). The transformation of HMF can be attributed to the in situ formation of the active component from DMSO at high temperature, the reaction pathway involves the protonation of the alcohol group of HMF and nucleophilic addition of DMSO, as reported in literature.[44] To test the aerobic catalytic ability of GO, the aforementioned reaction mixture was heated to 140 ^{o}C in the presence of 5 mg GO, after 24 h, the analysis of the product showed that up to 68.7% HMF conversion with 58.0% DFF yield was obtained (Table 1, entry 3). Increasing the GO amount to 10, 15, 20 mg in the reaction, HMF conversion increased to 83.4%, 92.5% and 100% with DFF yield to 70.6%, 78.6% and 90.0%, respectively (Table 1, entries 3-6). To determine whether the GO presents its catalytic activity by accelerating the thermolysis of DMSO, thus increasing the amount of in situ formation of active strong acids and HMF oxidation rate, the aforementioned reaction was conducted in DMF solvent, instead of DMSO. In the absence of GO, the in situ formed formic acid from DMF induced degradation of HMF with HMF conversion of 45.7% achieved, but no DFF was observed (Table 1, entry 7). However, the introducing of GO into the reaction led to a DFF yield of 44.7%, indicating that the presentation of GO catalytic activity does not depend on the DMSO solvent (Table 1, entry 8). ICP-AES analysis showed that GO contained an impurity of Mn element, around 300 ppm, which may be active sites in oxidation reactions.[16, 45] To check whether the impurity of Mn in GO is crucial for the aerobic oxidation, 4 mL DMSO with 0.02 mg $KMnO_4$ dissolved was used as the reaction medium, after 24 h at 140 ^{o}C, a HMF conversion of 39.0 % with a DFF yield to 27.2% were observed (Table 1, entry 9). Compared with the results catalyzed by GO (Table 1, entry 6) and the blank test (Table 1, entry 2), this result indicates the active sites originated from GO, instead of the residual Mn element in GO.

To confirm the role of carboxylic acid groups in oxidation reaction,[38, 41] 1-pyrene carboxylic acid was used as a molecular analogue to mimic the GO catalyst and a 79.3% HMF conversion with a 58.6 % DFF yield were obtained when 1-pyrene carboxylic acid was used in HMF oxidation reaction (Table 1, entry 10). These results demonstrate that carboxylic acid groups in GO material were responsible for the activation of molecular oxygen, corresponding to previous related reports.[38, 41]

Next, to determine whether the molecular oxygen was activated and participated in the HMF oxidation, the aforementioned reaction was performed in N_2 flow. After 24 h at 140 ^{o}C, the reaction products afforded less than 2 % HMF conversion (Table 1, entries 11-12). Underscoring the importance of the oxygen, continually heating of this reaction mixture under oxygen flow at 160 ^{o}C, the highest DFF yield of 78.1% with full HMF conversion was obtained in 9 h (Table 1, entry 13). Though higher temperature is benefit to shorten the reaction time, considering the DFF selectivity and energy consumption in operation, 140 ^{o}C was chosen as the reaction temperature in following tests. In all HMF oxidation tests, it was observed that FFCA was produced as a main byproduct and its yield ranged from 5-20 %. The carbon balance remained above 90 %.

2.2 Catalytic Dehydration of Fructose to HMF over GO.

In a preliminary experiment, 2 mmol fructose (360 mg) dissolved in 4 mL DMSO was heated to 140 ^{o}C in the presence of 20 mg GO under N_2 flow atmosphere. The catalytic behavior of GO in fructose dehydration was shown in Figure 1.

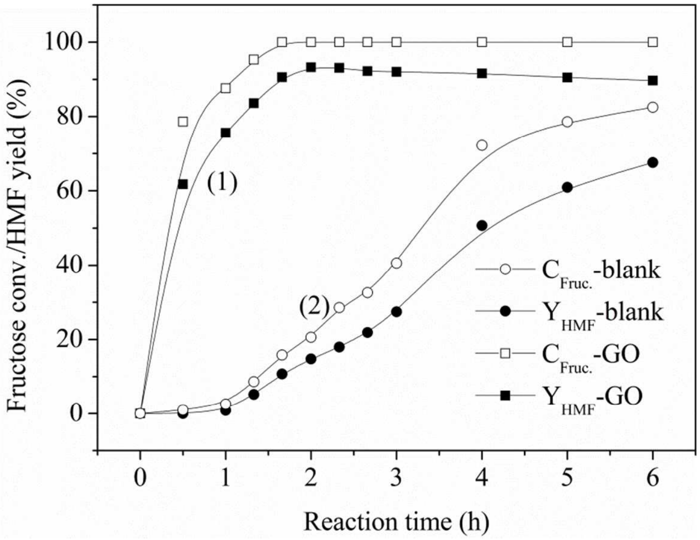


Figure 1. Comparison of fructose dehydration reaction catalyzed by GO and blank experiment. Reaction condition: (1) fructose, 2 mmol, 360 mg; DMSO, 4 mL; GO, 20 mg; T, 140 ^{o}C; N_2, 20 mL min^{-1}. (2) fructose, 2 mmol, 360 mg; DMSO, 4 mL; T, 140 ^{o}C; N_2, 20 mL min^{-1}.

As mentioned above, the in situ thermolysis of DMSO at high temperature can generate strong acids that could show catalytic ability at some extent in fructose dehydration.[44] In Figure 1, the blank experiment without any additive acid catalyst in neat DMSO showed that fructose conversion and HMF yield increased with reaction time. A 21.6 % fructose conversion and 17.8% HMF yield were obtained in 2 h, and up to 82.5 % fructose conversion and 67.5% HMF yield were obtained in 6 h. Addition of GO promoted fructose conversion to 100 % quickly, and up to 93.2 % HMF yield was obtained in 2 h (Figure 1). These results imply that the addition of GO can act as a catalyst in the conversion of fructose to HMF. In our previous work, [34] it was shown that a small number of sulfonic groups and abundant of oxygen-containing groups have an important synergic effect in maintaining the high performance of graphene oxide. The sulfonic groups are demonstrated to be the active sites and oxygen-containing groups in GO facilitate the adsorption of fructose on GO. Characterization of the GO catalyst by diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) and (TG-MS) shows that the sulfate groups on GO are stable even at 215 °C. At relative low temperature treatments (< 200 °C), most of the oxygen-containing groups that account for the majority of the acid sites on GO also remains stable. [34] Those results suggest that GO can be an efficient and recyclable carbon catalyst in fructose dehydration reaction.

Table 2. Fructose dehydration to HMF over different acid catalysts.[a]

Entry	Catalyst	Fructose Conv. (%)	HMF Yield (%)
1	---	21.6	14.7
2	GO	100	93.2
3[b]	HCl	100	97.5

4[c]	$H_3PW_{12}O_{40}$	100	97.4
5[d]	H-ZSM-5 (Si/Al=17)	100	77.4
6[d]	Hβ (Si/Al=20)	100	71.1
7[d]	USY-zeolite (Si/Al=12)	100	74.3
8[d]	SAPO(Si/Al=0.32)	100	78.8

[a] Reaction condition: fructose, 360 mg; GO, 20 mg, acid density (determined by Boehm titration method), 4.38 mmol NaOH/ g of GO; DMSO, 4 mL; T, 140 °C; t, 2 h, N_2, 20 mL min^{-1}.

[b] 0.0876 mmol HCl was used in reaction.

[c] 0.0292 mmol $H_3PW_{12}O_{40}$ was used in reaction (0.0876 mmol equiv of $H^{+.}$).

[d] 20 mg zeolite with different Si/Al ratio was used as the catalyst.

As listed in Table 2, GO shows promotion effect in fructose dehydration reaction (Table 2, entries 1, 2). The reactivity of GO was further compared with traditional Bronsted and Lewis acids, such as HCl, $H_3PW_{12}O_{40}$, and zeolites with different ratio of Si/Al. The GO acidity density was determined by Boehm titration method (Supporting information), and HCl and $H_3PW_{12}O_{40}$, equalling to the GO acidity concentration, were introduced into reaction system respectively. After the reaction mixture was heated at 140 °C for 2 h, full fructose conversion was achieved over all additive catalysts (Table 2, entries 2-8). Results show that the catalytic activity of GO is comparable to HCl and $H_3PW_{12}O_{40}$. Inferior catalytic behaviors were observed and a HMF yield of ~70-80% was obtained in Lewis acid catalytic system (entries 5-8).

According to the literature, the Lewis acidity of zeolites decreases the HMF selectivity by a fast initial condensation of fructose over the Lewis acid sites.[24]

2.3 One-pot Conversion of Fructose to DFF

2.3.1 One-pot, One-step Conversion of Fructose to DFF

The one-pot and one step synthesis of DFF from fructose was investigated with GO as the bifunctional catalyst. In a preliminary experiment, 2 mmol fructose dissolved in 4 mL DMSO was heated to 140 °C in the presence of 20 mg GO under a constant oxygen flow with a rate of 20 mL min^{-1}.

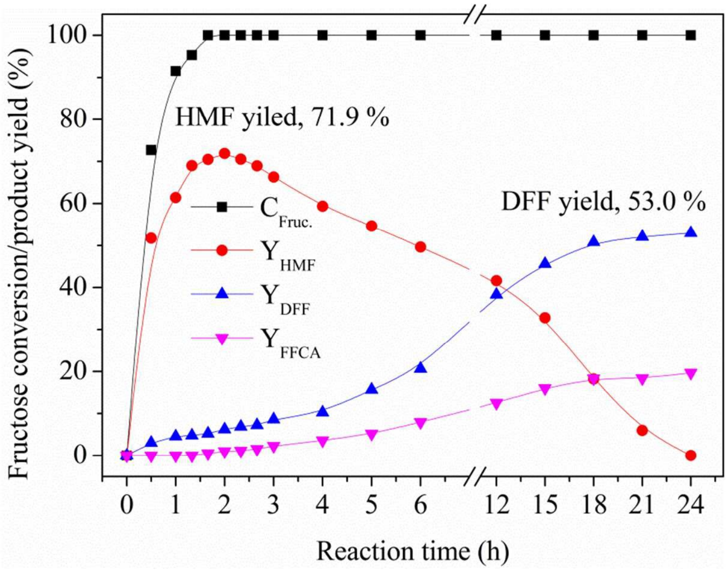


Figure 2. One-pot, one-step synthesis of DFF from fructose with GO as bifunctional catalyst. Reaction condition: fructose, 2 mmol, 360 mg; DMSO, 4 mL; GO, 20 mg; T, 140 °C; O_2, 20 mL min^{-1}.

Figure 2 shows the reaction profiles of one-pot, one-step process with GO as the bifunctional catalyst for DFF directly synthesizing from fructose. Results from analysis of reaction mixture indicate that there are three main products, HMF, DFF and FFCA. The HMF yield reached the maximum of 71.8 % with a carbon balance of

79.1% in 2 h. The lower carbon balance can be attributed to the undesired oxidation of fructose by GO in the presence of molecular oxygen from the initial stage of the reaction, which is also observed in other redox catalytic system.[4, 6, 24] Continued heating of the reaction mixture under O_2 flow afforded full HMF conversion after another 22 h. The highest DFF yield of 53.0% was achieved in 24 h. FFCA, a main byproduct, was also detected with a yield of 19.7 % in 24 h. After the reaction, the mixture was heavily colored, it is speculated that the low carbon balance (72.7%) was attributed to de degradation of HMF and the formation of humins over acidic GO, and the oxidation of fructose in the initial stage.

2.3.2 One-pot, Two-step Conversion of Fructose to DFF

According to related reports of one-pot synthesis of DFF from fructose, the co-existence of molecular oxygen with a redox catalyst in the initial reaction stage always induces the oxidation of fructose, which results in other undesired byproducts and the decrease of target products [4, 6, 17, 24, 46]. To reduce undesired fructose oxidation reactions, the one-pot reaction was performed under a N_2 flow for 2 h and subsequent O_2 flow for another 22 h.

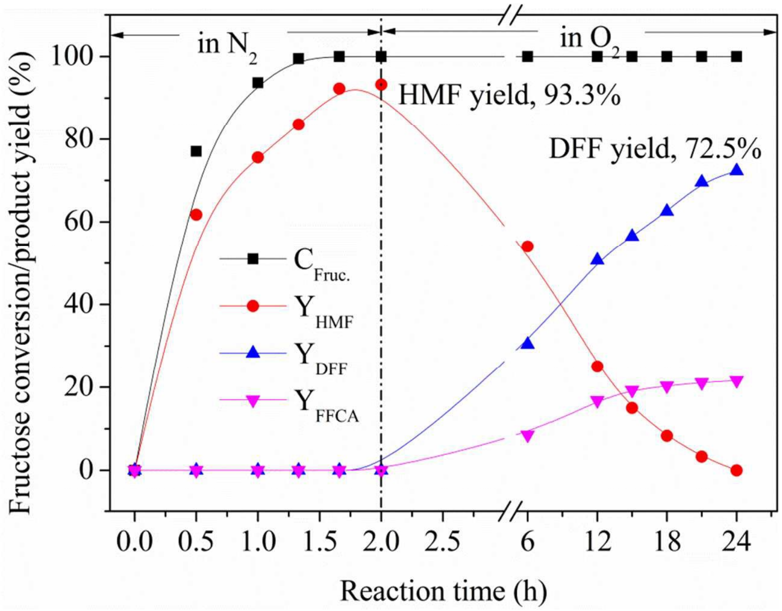


Figure 3. One-pot, two-step synthesis of DFF from fructose with GO as a bifunctional catalyst. Reaction condition: fructose, 2 mmol, 360 mg; DMSO, 4 mL; GO, 20 mg; T, 140 ^{o}C; N_2 or O_2, 20 mL min^{-1}.

As shown in Figure 3, a highest HMF yield of 93.3% was achieved after 2 h and no DFF or FFCA was observed after reaction for 2 h under N_2 atmosphere. The atmosphere change of N_2 to O_2 ignites the HMF oxidation. Catalyzed by GO under O_2 atmosphere, HMF disappeared gradually, and the DFF yield increased to an maximum of 72.5% after another 22 h. 21.6% yield of FFCA was observed. Thus, the results showed that GO can be used an efficient bifunctional catalyst in the direct synthesis of DFF from fructose by controlling the reaction atmosphere.

2.4 Reusability and Characterization of GO Catalyst

The reusability and stability of GO was investigated in the one-pot and two-step synthesis of DFF from fructose under identical conditions as described in Figure 3. After reactions, the heterogeneous GO material was separated from the reaction mixture by filtration, and washed by methanol and acetonitrile (100 mL ×5), respectively. Then the washed GO was dried in an oven at 60 ^{o}C for 12 h. By analysis of the HMF yield after 2 h under N_2 atmosphere and DFF yield after another 22 h under O_2 atmosphere, it was found that there was only a little drop of the GO catalytic activity as a bifunctional catalyst in one-pot fructose conversion after five runs (Figure S3, Supporting information). After 5 cycles, the morphology of graphene sheets did not exhibit noticeable differences under SEM and TEM observations, as shown in Figure S4.

In our another work with GO as an acid catalyst used in fructose dehydration [34] and one pot conversion of carbohydrates into 5-ethoxymethylfurfural,[35] it was observed that GO underwent partial reduction after long time exposure at high temperatures. It also has been demonstrated that in aerobic oxidation reactions with GO as an carbocatalys,[20, 33, 38] GO would function as an oxidant and become reduced at the end of the first catalytic cycle, and the partially reduced GO material could then be the real catalyst for molecular oxygen activation. Similar behavior of GO was also observed in our previous work in aerobic oxidation of HMF into DFF with GO as the carbocatalyst.[41] XPS analysis of the fresh and spent GO catalyst after 5 cycles confirmed this speculation. As shown in Figure S5, Figure S6 and Table S1 (in supporting information), the ratio of C/O increased from 1.49 to 2.39 and all the oxygen groups content decreased to some extent. Additionally, the C, O, H, and S contents of spent GO have been tested (Table S2, Supporting information). The S content in spent GO was 3.2 wt %, and the O content decreased to 27.3 wt %.

Compared with the fresh GO, a slight increase of the S content in spent GO was observed. This can be attributed to the interaction between the GO and the in situ formed acids by thermolysis of DMSO at high temperature, which induced the strong adsorption of acids on GO or connected to GO by covalent bond. However, the detailed mechanism of the reaction between GO and high temperature DMSO is still unclear. Collectively, these results suggested to us that the GO catalyst underwent partial reduction during the conversion of fructose to DFF and afforded a carbon product that was similar to the r-GOs and CMGs that had been previously observed in other reactions.[20, 27, 38] Thus, the little loss of GO reactivity as bifunctional catalyst in one-pot synthesis of DFF from fructose can be attributed to the partial reduction of some oxygen-containing groups during catalytic reaction.

3. Conclusion

Based on the catalytic properties of GO, that is, the synergic effect of sulfonic groups with oxygen-containing groups in catalyzed fructose dehydration reaction and the selective dehydrogenation function derived from the synergic effect of carboxylic acid groups with the unpaired electrons at the GO edge defects, we discovered that GO synthesized from Hummer’s method can be used as a simple, efficient and easy recycled bifunctional and metal-free catalyst in the one-pot synthesis of DFF from fructose. GO showed excellent catalytic activities in acid catalyzed fructose dehydration reaction as well as redox catalyst catalyzed aerobic HMF oxidation reaction. Catalyzed by GO, a HMF yield of 93.2 % from fructose dehydration and a DFF yield of 90.0% from aerobic oxidation of HMF were achieved, respectively.

Besides, the one-pot and one-step method produced DFF in a yield of 53.0%, whereas the two consecutive method (N_2 and O_2) improved the DFF yield to 72.5%, based on fructose.

With dwindling supplies of the precious metals used in common catalysts, the prospect of replacing these metals with inexpensive carbon materials is extremely attractive and timely. Furthermore, the integrated process for the production of DFF direct from fructose is promising from both a green and sustainable chemistry perspective.

Associated Content

Supporting information: Experimental details, GO preparation and characterization. Effect of other polarity solvents in fructose transformation. Figure S1-S6, Table S1-S3.

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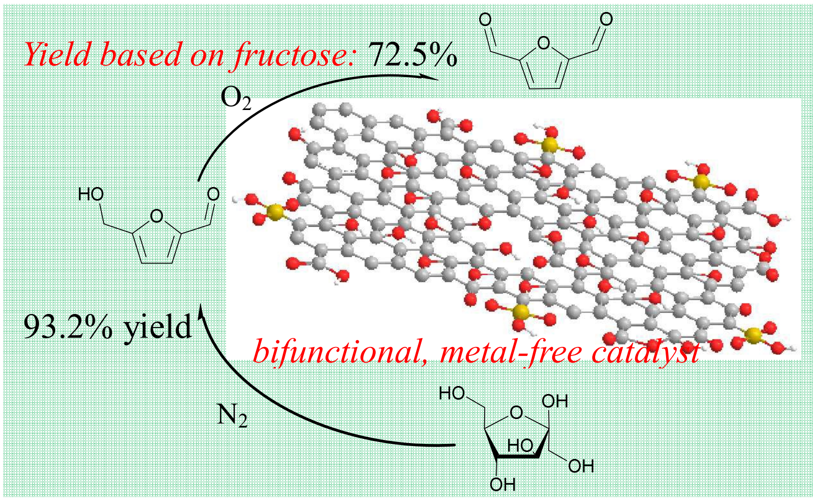
Yield based on fructose: 72.5%
O2
HO
O
O
O
O
93.2% yield
bifunctional, metal-free catalyst
N2
HO
O
OH
HO
OH
OH