



Selective oxidation of biomass derived 5-hydroxymethylfurfural to 2,5-diformylfuran using sodium nitrite[☆]

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ABSTRACT

A mild and simple process for the effective oxidation of 5-hydroxymethylfurfural (HMF) into 2,5-diformylfuran (DFF) has been developed using NaNO₂ as the oxidant. Some important reaction parameters were investigated to optimize the oxidation of HMF into DFF. It was found that the reaction solvent was very crucial for this reaction. Trifluoroacetic acid was the best solvent for the oxidation of HMF into DFF by NaNO₂. Under the optimal reaction condition, almost quantitative HMF conversion and high DFF yield of 90.4% were obtained after 1 h at room temperature.

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1. Introduction

Nowadays, the conversion of renewable biomass resources into chemicals and fuels has received a growing interest, as it can substitute fossil resources to improve the sustainability of the chemical industry [1–4]. Carbohydrates represent the major component of biomass. The catalytic conversion of carbohydrates can produce many useful chemicals and fuels [5,6]. Among them, the dehydration of C₆ based carbohydrates can generate an important platform chemical 5-hydroxymethylfurfural (HMF), which is considered to be one of the top value-added chemicals [7,8]. HMF can be used as a versatile precursor for the production of high energy-density biofuels and useful chemicals. Fruitful results have been achieved for the synthesis of HMF from various carbohydrates such as fructose, glucose, and cellulose [9–12].

Currently, great effort has been devoted to the transformation of HMF into HMF derivatives. Through oxidation reaction, several useful furan compounds can be obtained [13–15]. For example, 2,5-furandicarboxylic acid (FDCA) has been identified as one of the 12 chemicals US Department of Energy biomass program [16]. It can

be replaced with petroleum-derived chemical building blocks such as terephthalic, isophthalic, and adipic acids, which have been widely used for the production of key polymers such as polyethylene terephthalate (PET) and polybutyleneterephthalate (PBT) plastics [17].

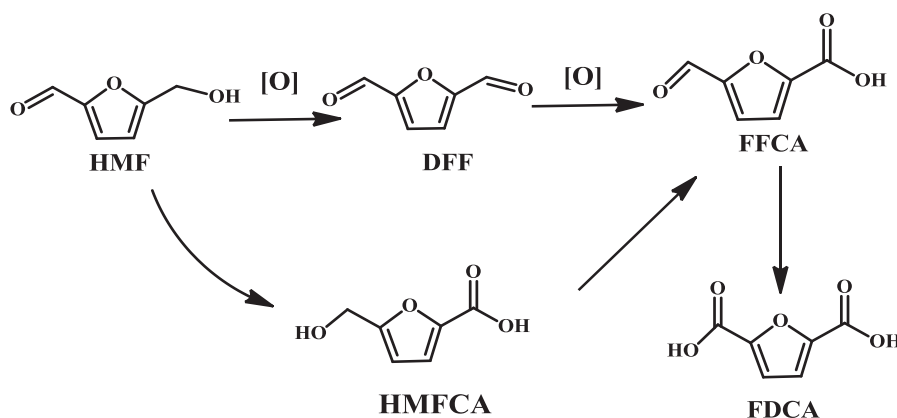
2,5-Diformylfuran (DFF), as another oxidation product of HMF, has also been found to be useful in many fields [18–21]. It can be used as a precursor for the synthesis of pharmaceuticals, macrocyclic ligands, and renewable furan–urea resin. DFF can be prepared through partial oxidation of the hydroxymethyl group in HMF, which is similar as the oxidation of primary alcohols bearing an aromatic moiety. However, as shown in Scheme 1, HMF molecule contains two functional groups including hydroxyl and aldehyde functionalities. Therefore, the oxidation of HMF makes it susceptible to undergo many side reactions such as over-oxidation of DFF into FDCA, the oxidation of aldehyde to 5-hydroxymethyl-2-furancarboxylic acid (HMFA), decarbonylation, and cross polymerization to produce unwanted byproducts. Therefore, it is still a challenge to selectively oxidize HMF into DFF.

In early reports, the oxidation of HMF into DFF was carried out by the use of the traditional oxidants such as NaOCl and pyridinium chlorochromate [22–24]. However, those methods have some distinct drawbacks such as the release of toxic waste and the high cost of the oxidants. In recent years, it is recognized that the oxidation of HMF can be performed using molecular oxygen as terminal oxidant. Partenheimer et al. reported that catalytic oxidation of HMF by homogenous metal bromide catalysts (MBr₂, M = Co(II)/Mn(II)/Zr(II)) at 70 bar oxygen pressure gave 99.7% of HMF conversion with 61% of DFF selectivity [25]. Recently, some heterogeneous catalytic systems have been developed for the oxidation of HMF [26–28]. For

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Scheme 1. Possible oxidation products from the oxidation of HMF.

example, Sádaba et al. recently reported that the aerobic oxidation of HMF catalyzed by zeolite-supported vanadium gave rise to high DFF selectivity of 99% and HMF conversion of 84% under 10 bar oxygen pressure [26]. Acknowledging these important achievements, many of the present protocols required high reaction temperatures (up to 150 °C), and high oxygen pressure (up to 10 bar) to ensure desirable DFF selectivity at high HMF conversion. Therefore, it is still required to develop new method for the oxidation of HMF into DFF under mild reaction conditions.

Sodium nitrite (NaNO_2) is a cheap and commercially available chemical, which has been shown as a strong oxidant in many oxidation reactions [29,30]. For example, the oxidation of primary alcohols to aldehydes was effective by the use of NaNO_2 as the oxidant in the solvent of acetic anhydride [31]. It also reported that oxidation of aliphatic cycloalkanols by sodium nitrite in trifluoroacetic acid gave dicarboxylic acids in good yields [32]. Herein, in this study, we would like to study the oxidation of HMF by the use of sodium nitrite as the oxidant. To our surprise, high HMF conversion and DFF selectivity were obtained under our reaction conditions.

2. Experimental

2.1. Materials

NaNO_2 was purchased from Aladdin Chemicals Co. Ltd. (Beijing, China). All of the solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 2,5-diformylfuran was purchased from the J&K Chemical Co. Ltd., (Beijing, China). 5-hydroxymethylfurfural (98%) was supplied by Beijing Chemicals Co. Ltd. (Beijing, China). Acetonitrile (HPLC grade) was purchased from Tedia Co. (Fairfield, USA).

2.2. General procedures for the aerobic oxidation of HMF to DFF

In a typical run: oxidation of HMF was carried out in a 10 mL round bottom flask, which was coupled with a reflux condenser and capped with a balloon. First, HMF (0.8 mmol, 100 mg) was added into trifluoroacetic acid (4 mL), and the mixture was stirred vigorously to give a clear solution. Then NaNO_2 (55.2 mg, 1 equiv) was added into the above mixture. The reaction was carried out at 25 °C with a mechanical stirring at a speed of 600 rpm. Time zero was recorded after the addition of NaNO_2 in the reaction solution. At different reaction time points, a little sample was withdrawn from the reaction solution and analyzed by HPLC.

2.3. Analytic methods

Furan compounds were analyzed on a VARIAN ProStar 210 HPLC system. Samples were separated by a reversed-phase C18 column

Table 1. The results of the oxidation of HMF into DFF in different solvents.

Entry	Solvent	HMF conversion (%)	DFF yield (%)	FDCA yield (%)
1	Trifluoroacetic acid	98.3	89.8	6.3
2	Dimethyl sulfoxide	1.5	0.6	0.3
3	Ethanol	1.2	0.7	0.4
4	Acetic acid	1.2	0.8	0.3
5	H_2O	1.7	1.4	0.5
6	Acetonitrile	1.6	1.5	0.3
7 ^a	$\text{H}_2\text{O} + \text{H}_2\text{SO}_4$	1.7	3.2	1.5

Reaction conditions: HMF (100 mg) was dissolved in 4 mL of solvent, and then NaNO_2 (82.8 mg, 1.5 equiv) was added into. The reaction mixture was stirred at room temperature for 1 h.

^a 2 mL H_2SO_4 and 2 mL H_2O was used.

(200 × 4.6 mm) and detected by UV detector at a wavelength of 280 nm. The mobile phase was constituted of acetonitrile and 0.1 wt% acetic acid aqueous solution with a volume ratio of 30:70. The flow rate was set at 1.0 mL/min. The column oven temperature was kept at 25 °C. The content of HMF and DFF in samples was calculated by the external standard calibration curve method, which was constructed based on the pure compounds.

$$\text{HMF conversion (\%)} = \frac{\text{Moles of converted HMF}}{\text{Moles of starting HMF}} \times 100\%$$

$$\text{DFF yield (\%)} = \frac{\text{Moles of DFF}}{\text{Moles of starting HMF}} \times 100\%$$

3. Results and discussion

3.1. Oxidation of HMF into DFF over NaNO_2 in different solvents

Generally speaking, the reaction solvent plays a key role in the chemical reaction, as the different solvents have different properties such as the polarity, dielectric constant, steric hindrance, acid–base property [33]. Therefore, the oxidation of HMF was initially carried out in various solvents to study the solvent effect. Table 1 shows the results of HMF oxidation in each solvent by the use of NaNO_2 . As shown in Table 1, the reaction solvent greatly affected the oxidation of HMF. Trifluoroacetic acid was found to be the best solvent. High HMF conversion of 98.3% and DFF yield of 89.3% were obtained after 1 h at the reaction temperature of 25 °C with trifluoroacetic acid as the solvent (Table 1, Entry 1). However, other solvents were very inferior for the oxidation of HMF using NaNO_2 as the oxidant (Table 1, Entries 2–6). Negligible HMF conversion and product yield were observed when the oxidation of HMF was carried out in other solvents (Table 1, Entries 2–6). The distinct difference between trifluoroacetic acid and other solvent is that trifluoroacetic acid is a strong acid. It is

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