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#### Supporting information

# Selective oxidation of 5-hydroxymethylfurfural to diformylfuran in the presence of Oxone and catalyzed by 2-iodobenzenesulfonic acid

#### -Materials and methods:

Typical oxidation of HMF:

All the oxidation reactions were performed in a reactor, which was coupled to a reflux condenser, oil bath heater and a magnetic stirrer (stirring speed of 600 rpm). 6 mL of solvent, the catalyst sodium 2-iodobenzenesulfonate (30mg) and 1.17 g of well grinded Oxone<sup>®</sup> were added in the reactor, as soon as the set temperature is reached, the HMF was introduced (200 mg, 1,58 mmol) in the reactor. Immediately after, the reactor was cooled to room temperature, the organic phase was recovered by adding ethyl acetate, washed with water to dissolve any potassium salt traces and then the phases were separated. The residual Oxone<sup>®</sup> salts were simply filtered and rinsed with ethyl acetate. The combined organic phases were evaporated under reduced pressure, and the recovered product was diluted with ethyl acetate in volumetric flask to be analyzed by Gas Chromatography (GC) and NMR.

## -Catalyst Recovery after HMF Catalyzed Oxidation Reactions:

After following the typical procedure of oxidation of HMF. The resulting mixture was cooled to room temperature and filtered through a plug of tightly packed celite, which was successively washed with EtOAc, and removed of solvents in vacuum to give crude mixture which containing catalyst derivatives. To this crude mixture was added diethyl ether (2–4 mL) and iodines derivatives were precipitated. After simple filtration, pH acidic precipitates were obtained in 50%. Alternatively, the reaction mixture is basified by adding an aqueous solution of sodium hydrogencarbonate. Then the DFF is extracted with ethyl acetate. The aqueous phase containing the sulfate salts and the catalyst is then acidified and the catalyst extracted with ethyl acetate four times. The solvent is evaporated and the catalyst is recovered.

### - Catalyst synthesis method

By following the method developed by Ishiha100ra and al.<sup>1</sup> To a stirred suspension of 2aminobenzenesulfonic acid (5.0 g, 28.9 mmol) and crushed-ice (20 g) in concentrated HCl (10 mL) was added NaNO<sub>2</sub> (2.09 g, 30.3 mmol) in water (10 mL) slowly at 0 °C, and stirred for 20~30 min at below 5 °C. (Immediate precipitation of the diazonium salt was observed). A solution of NaI (4.76 g, 31.76 mmol) in water (10 mL) was then added slowly with stirring at 0 °C. After addition was complete, stirring was continued at 0 °C for 1 h, at room temperature for 1 h and at 50 °C for 12 h to remove all N2. The mixture was than refrigerated, and the insoluble component was separated. After the solid was treated with boiling EtOH (some Et2O and MeOH then added), the mixture was allowed to cool to separate the insoluble solid. The solid was washed with cold EtOH and Et<sub>2</sub>O to isolate as the monohydrate of Sodium 2-lodobenzenesulfonate

#### - Methodology of Experiments

All of the reagents are analytical grade and were used without further purification. All products or solvents and reagents were purchased either from Fischer Scientific or Merck. NMR analysis of the products were conducted on a Brucker Ascend<sup>TM</sup> 400MHz device. The samples were prepared in deuterated water, DMSO, CD<sub>3</sub>OD or chloroform depending on their solubility. All products were analyzed and quantified by gaz chromatography Perkin Elmer instruments, AutoSystem XL Gas Chromatography. Column Alltech Part No. 16368 AT-1ht 30m x 0.25mm D x 0.1um. injection volume 1ul, oven temperature: 40°C for 2 min, then increasing by 20°C/min till 250°C, and the temperature stays constat for 3 min,  $Q_{H2}$ = 45 ml/min and  $Q_{air}$ =450 ml/min. Retention time of DFF: 6.9 min, HMF: 8.2 min. Furthermore some samples were analyzed by HPLC-MS (UFLC Shimadzu) with a diode array detector (Shimadzu SPD-M2OA) an evaporative light scattering detector (Shimadzu ELSD-LTII) and coupled to mass spectrum detector (Shimadzu LCMS 2020). The HPLC instrument was equipped with a GRACE Prevail C18 5µ column (250 mm \* 4.6 mm). The mobile phase was: Eluent CH<sub>3</sub>CN-H<sub>2</sub>O with 0,01 mol.dm<sup>-3</sup> Na<sub>2</sub>HPO<sub>4</sub> (1/9), pH was adjusted to 2.4 with H<sub>3</sub>PO<sub>4</sub> at a flowing rate of 1 ml.min<sup>-1</sup>. Temperature of the column was 303K. The injection volume was 5 µL. Before injection, all samples of reaction mixture were filtered through a 0.45 µm syringe filter.

#### RMN of diformylfuran:

<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ/ppm 7.73 (s, 1H), 9.874 (s, 1H); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ/ppm 122.06 (13C), 153.59 (2C), 180.68 (2C). Products are dissolved in Deuterated DMSO for analysis.

HRMS (ESI-MS+) Exact mass = 124.0524297 Calculated mass = 124.01521

#### Gram scale synthesis of DFF:

<u>Reaction procedure:</u> The gram-scale oxidation reaction was performed in a three necks flask, which was coupled to a reflux condenser, an oil bath heater and a magnetic stirrer (stirring speed of 600 rpm). 60 mL of solvent, the catalyst sodium 2-iodobenzenesulfonate (300 mg) and 11.7 g of well grinded Oxone<sup>®</sup> were added in the reactor, as soon as the set temperature (70°C) is reached, the HMF was introduced (2 g) in the reactor for 4 hours. At the end of the reaction, about 100 mL of ethyl acetate were added in the reactor. Then, the mixture was transferred in a separatory funnel by filtrating the residual sulphate salts that settle out at the bottom of the reactor. The insoluble sulphate salts were washed with ethyl acetate and organic phases were combined. The organic phase was washed with 3 times 40 mL of water and the aqueous phase was discarded. The organic layer was then evaporated and 1.78 g of DFF was recovered as a yellowish-white powder (Yiled = 87%). The DFF was further analyzed by GC, NMR.

#### DFF yield and HMF conversion determination:

After the recovery of DFF, a specific amount was taken from the total recovered mass, then diluted in ethyl acetate and injected in the GC. The surface under HMF and DFF peaks were measured. Using the calibration curves of DFF and HMF, concentrations of DFF and HMF in the diluted solutions, therefore their mass, were determined. HMF conversion and the DFF yield and selectivity were calculated using these equations:

 $HMF \ conversion = \frac{n_{HMF_{initial}} - n_{HMF_{remaining}}}{n_{HMF_{initial}}} \times 100$ 

 $DFF \ yield = \frac{n_{DFFobtained}}{n_{DFFtheoretical}} \times 100$ 

 $DFF \ selectivity = \frac{n_{DFFobtained}}{n_{HMF_{initial}} - n_{HMF_{remaining}}} \times 100$ 

#### -NMR Spectra of DFF, over-oxidation product and catalyst:



Figure 1-1H spectrum of DFF after filtration and evaporation



Figure 2- 13C spectrum of DFF after filtration and evaporation



Figure 3-1H spectrum of over-oxidation



Figure 4-13C spectrum of over-oxidation



Figure 5- 1H spectrum of the catalyst



Figure 6- 13C spectrum of the catalyst



Figure 7-1H spectrum of the gram scale oxidation



Figure 8-13C spectrum of the gram scale oxidation



# -Some related GC chromatograms

1.5 2.0 2.5 2.0 2.5 4.0 4.5 7.0 7.6 12.5 11.0 11.5 12.0 12.6 13.0 13.6 14.0 14.5 15.0 0.5 1.0 5.0 1. 8.0 1. 8.0 1.5 9.0 9.5 10.0

Figure 9- Chromatogram of DFF after filtration and evaporation



Figure 10- chromatogram of HMF oxidation without catalyst



Figure 11- chromatogram of HMF oxidation without solvent

## -IR and HRMS spectra for the gram-scale reaction



Figure 12- FTIR spectrum of the gram-scale oxidation



Figure 13- HRMS (ESI-MS+) spectrum of the gram scale oxidation

**Exact mass =** 124.0524297 **Calculated mass =** 124.01521