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#### Biomimetic oxidase based on functionalized mesoporous SiO<sub>2</sub> and

#### metalloporphyrin for 5-hydroxymethylfurfural conversion

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# Metal porphyrin as active center of oxidase is deeply buried in glycoprotein

#### Highlights

**Graphical abstract** 

5-hydroxymethylfurfural(HMF) oxidation was carried out in aqueous phase.

- Metal porphyrin as biomimetic oxidase catalyzed HMF conversion.
- Excellent HMF conversion of 100% and FDCA yield of 94.94% were achieved.

#### **Abstract:**

2,5-furandicarboxylic acid (FDCA) has the potential to replace terephthalic acid (TPA) as a building block in the preparation of bio-based and degradable polyester materials. However, the lack of efficient and stable catalysts limits the commercial viability of FDCA production. In this work, metalloporphyrins were immobilized on mesoporous SiO<sub>2</sub> and used as a novel oxidase to convert 5-hydroxymethylfurfural (HMF) to FDCA. As the catalytic active center of P450 monooxygenases and horseradish peroxidase, supported palladium, manganese, ferri, and cobalt porphyrins via ionic-liquid-functionalized SiO<sub>2</sub> (PdPOP-SiO<sub>2</sub>, MgPOP-SiO<sub>2</sub>, FePOP-SiO<sub>2</sub> and CoPOP-SiO<sub>2</sub>) were able to simulate oxidase alone under mild conditions. 100% HMF (0.02 M) conversion and 94.94% FDCA yield were achieved using PdPOP-SiO<sub>2</sub> as a biomimetic oxidase after a 12 h reaction at 373 K in water at atmospheric pressure. This type of mimetic oxidase is stable, inexpensive, and readily available, and the method developed in this work can potentially be used to oxidize HMF to FDCA in an industrial setting.

**Keywords:** mimetic oxidase, functionalized surface, mesoporous, 5-hydroxymethylfurfural, 2,5-furandicarboxylic acid.

#### 1. Introduction

Renewable resources have received increasing attention to replace fossil fuels. Cellulose, one of the most abundant natural resources, can be transformed into 5-hydroxymethylfurfural (HMF) whose chemical structure contains a methylol group, a formyl group, and a furan ring<sup>[1]</sup>. HMF has been selected as a platform compound to generate more valuable chemicals through ring-opening, reduction, and oxidation reactions.<sup>[2, 3]</sup> Of the products derived from HMF, 2,5-furan dicarboxylic acid (FDCA) can be prepared through the full oxidation of HMF.<sup>[4]</sup> The molecular structure of FDCA is similar to that of terephthalic acid (TPA), which is derived from fossil oils and used to prepare polyethylene terephthalate (PET) plastics. Degradable FDCA from biomass could be used as a renewable replacement for TPA, which is generated at a rate of 45.2 million tons per year.<sup>[5, 6]</sup> Biomass-based FDCA could save energy, reduce trash, prevent pollution, and protect the environment, so it is very meaningful to investigate the oxidation of HMF into FDCA (**Scheme 1**).

The catalysts used in HMF aerobic oxidation have received significant attention from researchers. As early as 2012, Saha et al. catalyzed HMF oxidation using Co(OAc)<sub>2</sub>/Zn(OAc)<sub>2</sub>/NaBr as a homogeneous catalyst and obtained 60% FDCA yield.<sup>[7]</sup> Recently, Zuo et al. reported that Co/Mn/Br homogeneous catalysts boosted HMF oxidation with over 90% FDCA yield.<sup>[8]</sup> However, it is difficult to separate homogeneous catalysts from reaction systems for recycling, which greatly increases the production cost of FDCA. Hence it is preferable to use heterogenous catalysts, the catalytic efficiency of supported Au, Pd, Ru, and Pt have been shown to be

particularly effective.<sup>[9, 10]</sup> Rass et al. reported that 100% HMF conversion was obtained using a Pt/C catalyst with 70% FDCA yield at 373 K under 40 bar O<sub>2</sub> pressure.<sup>[11]</sup> Mei et al. obtained 52.7% HMF conversion and 45.8% FDCA yield using C-Fe<sub>3</sub>O<sub>4</sub>-Pd catalyst at 373 K in dimethyl sulfoxide.<sup>[12]</sup> In addition, Wang et al. reported that nano-Fe<sub>3</sub>O<sub>4</sub>-CoOx catalyzed HMF oxidation with 68.6% FDCA yield and 98.7% HMF conversion in dimethyl sulfoxide in 12 h, using tert-butyl hydroperoxide as the oxidant.<sup>[13]</sup> However, the above catalysts required high pressure, organic solvents, and strong oxidants, which resulted in environmental pollution. Therefore, the design of green, environmentally-friendly catalysts is crucial.

Porphyrin is a macrocyclic compound containing four pyrrole molecules, and when the pyrrole proton is replaced by a metal ion, it becomes a metalloporphyrin.<sup>[14]</sup> Metalloporphyrin, the catalytic active center of cytochrome P450 monooxygenase and horseradish peroxidase, is stable, has a strong specificity, is economical, and is readily available. It can simulate oxidase to activate molecular oxygen under mild conditions.<sup>[15-17]</sup> Currently, only two studies have reported the use of metalloporphyrins for HMF oxidation.<sup>[18-19]</sup> Saha et al reported that 100% HMF conversion was obtained using a porous polymer-immobilized Fe(III) porphyrin catalyst and oxygen as the oxidant to achieve a 79% FDCA yield at 373 K under 10 bar O<sub>2</sub> pressure in water after 10 h reaction.<sup>[18]</sup> Metalloporphyrins have been shown to be excellent catalysts for HMF oxidation, but the high pressure and low FDCA yield need further improvements. Gao et al. obtained 95.6% HMF conversion and 90.4% FDCA yield using a Merrifield-resin-supported Co(II) porphyrin catalyst and a tert-butyl hydroperoxide oxidant at 373 K in acetonitrile after 24 h reaction at atmospheric pressure.<sup>[19]</sup> However, the use of expensive tert-butyl hydroperoxide oxidant, organic solvents, and the long reaction time restrict the applications of Co(II)

porphyrin catalysts. Therefore, we envisage a novel catalyst based on metalloporphyrin that combines the advantages of both Fe(III) and Co(II) porphyrins.

In this study, palladium porphyrin, manganese porphyrin, ferriporphyrin, and cobalt porphyrin are investigated for use as biomimetic oxidases for HMF oxidation. Since homogeneous metalloporphyrins easily form dimers that are difficult to separate, recover, and reuse,<sup>[20, 21]</sup> metalloporphyrins were loaded onto mesoporous SiO<sub>2</sub>. Due to its large specific surface area, tunable pore size, and abundant modifiable -OH groups, mesoporous SiO<sub>2</sub><sup>[22]</sup> is an excellent support material for metalloporphyrins. The oxidation activity of oxidase is the result of the combination of metalloporphyrins and glycoproteins. Individual metalloporphyrin activity usually was low due to their naturally hydrophobic environment loss. When functionalized ionic liquids, one kind of designable ionic solvent, which could mimic glycoproteins, were introduced into the mesoporous SiO<sub>2</sub> surface, it provided the metalloporphyrin with a biomimetic microenvironment <sup>[23, 24]</sup>.

Therefore, metalloporphyrins were chosen as the active centers, mesoporous SiO<sub>2</sub> as the carrier, and an ionic liquid as a modifier for the oxidation of HMF (**Scheme 2**). The effect of four different metal ions (iron, cobalt, manganese, and palladium) on the catalytic activity of biomimetic oxidases was investigated. Then, the optimal catalyst was selected to investigate the effect of catalyst dosage, temperature, time, oxidant type, and amount of base on the catalytic conversion of HMF to FDCA. Furthermore, the reusability of this novel biomimetic oxidase was investigated to identify an excellent and green catalyst for HMF oxidation.

#### 2 Experiment

#### **2.1 Materials**

5-hydroxymethyl-2-furancarboxylic acid (HFCA), 5-formyl-2-furancarboxylic acid (FFCA), FDCA, and HMF were purchased from J&K Chemical Co. Ltd. 5,10,15,20-Tetra(4-pyridyl)porphyrin and palladium(II) chloride (PdCl<sub>2</sub>, 59%Pd) were purchased from Aladdin Chemicals Co. Ltd. Mesoporous silica was purchased from Qingdao Mei Gao Group Co. Ltd. (particle size 220 nm, pore diameter 11.5 nm). All other reagents, including cobalt acetate, anhydrous ferric chloride, manganese acetate, chloropropyltriethoxysilane, N,N-dimethylformamide (DMF), cyclohexane, and absolute ethanol were purchased from Sinopharm Chemical Reagents.

#### 2.2 Preparation of metalloporphyrins

Excess metal salts (cobalt acetate, manganese acetate, anhydrous ferric chloride, and palladium chloride) and 1 g 5,10,15,20-Tetra(4-pyridyl)porphyrin were added into a 250 mL flask with 50 mL DMF. The molar ratio of metal salt to porphyrin was 5: 1. The mixed solution was then heated in an oil bath at 433 K with 1000 rpm magnetic stirring for 12 h. Afterwards, the mixture was cooled to room temperature, and a rotary evaporator removed most of the solvent, and then 50 mL deionized water was added into the mixture. Finally, the mixture was filtered to obtain a solid catalyst, and the metal salts that did not participate in the reaction was washed with DMF.<sup>[18]</sup> The resulting solid catalysts (denoted as PdPOP, FePOP, MnPOP, and CoPOP) were dried at 353 K for 24 h and reserved for further use.

#### 2.3 Preparation of modified SiO<sub>2</sub>

First, pure mesoporous SiO<sub>2</sub> was activated in a vacuum oven at 473 K for 4 h for further use. Then, 5 g chloropropyl triethoxysilane was added into a 150 mL Erlenmeyer flask with 30 mL cyclohexane. After that, 5 g activated mesoporous silica was added into the solution, which was then sealed and stirred at 298 K with 1000 rpm magnetic stirring for 24 h. Finally, the reaction mixture was washed, filtered with

cyclohexane, and dried at 353 K for 24 h to give a white solid powder which was extracted with ethanol for 8 h to remove physically-adsorbed chloropropyl-functionalized silica.<sup>[25]</sup> The powder was dried at 353 K for 24 h to obtain the final functionalized silica sample for further use.

#### 2.4 Immobilization of metalloporphyrins on modified SiO<sub>2</sub>

Metalloporphyrins (iron porphyrin, cobalt porphyrin, manganese porphyrin, and palladium porphyrin) were mixed with 1 g chloropropyl functional mesoporous silica at a ratio of metalloporphyrins to chloropropyl-functionalized mesoporous silica of 0.74 mmol·g<sup>-1</sup>. Then, they were dissolved in 50 mL DMF and heated at 433 K with 1000 rpm magnetic stirring for 24 h.<sup>[26]</sup> Afterwards, the reaction solution was cooled to 298 K and filtered. Finally, the solid catalyst was washed with water and DMF and dried in a vacuum oven at 353 K for 24 h for further use. These samples were denoted as PdPOP-SiO<sub>2</sub>, FePOP-SiO<sub>2</sub>, MnPOP-SiO<sub>2</sub>, and CoPOP-SiO<sub>2</sub> (**Scheme 2**).

#### 2.5 Aerobic oxidation process of HMF over biomimetic oxidase catalysts

To test the effect of solvent, HMF (0.08 mmol, 10 mg) was first dissolved in 4 g solvent (deionized water, acetonitrile, ethanol, toluene, or dimethyl sulfoxide) in a reaction flask. A certain amount (20 mg, 40 mg, 60 mg, 80 mg, 100 mg) of immobilized metalloporphyrin mimetic enzyme catalysts (PdPOP-SiO<sub>2</sub>, FePOP-SiO<sub>2</sub>, MnPOP-SiO<sub>2</sub>, and CoPOP-SiO<sub>2</sub>) and NaOH (0 mg, 2 mg, 4 mg, or 6 mg) were quickly added to the reaction system, and oxygen was passed through the reaction mixture(10 ml/min). The reaction mixture was sealed immediately and was as immersed in an oil bath at the desired temperature (313 K, 333 K, 353 K, 373 K, or 393 K) with stirring at 500 rpm. After a desired reaction time (2 h, 4 h, 8 h, 12 h, or 24 h), a 10  $\mu$ L aliquot was collected from the reaction solution and analyzed by high-performance liquid chromatography (HPLC). The catalyst used in the experiment

was filtered to remove the supernatant. Used catalysts were washed twice with deionized water and dried at 353 K for 24 h to recover the catalyst for reusability testing.

Reactants and products were analyzed by HPLC (Shimadzu Technology, model 20AB) equipped with an ultraviolet (UV) detector. Samples were measured at a wavelength of 280 nm using a reverse-phase Sapphire C<sub>18</sub> column from Sepax Technologies, inc. (200 mm  $\times$  4.6 mm, PN 801185-4625). The mobile phase for gradient elution analysis was composed of acetonitrile and 0.1wt% acetic acid aqueous solution at a 0.5 mL·min<sup>-1</sup> flow rate. The concentration of FDCA, HFCA, FFCA, and HMF (retention time was 10.2, 11.1, 12.3, 15.1 min respectively.) were calculated from the calibration curves of standards as follows:

HMF conversion = converted HMF moles/initial HMF moles  $\times$  100%.

HFCA yield = HFCA moles/ initial HMF moles  $\times$  100%.

FFCA yield = FFCA moles/initial HMF moles  $\times$  100%.

FDCA yield = FDCA moles/initial HMF moles  $\times$  100%.

#### 3. Results and discussion

#### **3.1.** Catalyst characterization

In this study, the preparation of biomimetic oxidases included three reaction steps. Firstly, the metalloporphyrins were synthesized by reacting metal salts with 5,10,15,20-Tetra(4-pyridyl)porphyrin. Secondly, mesoporous SiO<sub>2</sub> was modified by chloropropyl triethoxysilane. Finally, metalloporphyrins were grafted onto modified SiO<sub>2</sub> via ionic liquid bonding (**Scheme 2**). Scanning electron microscopy (SEM) was used to analyze the particle size and morphological changes of the SiO<sub>2</sub> carrier and metalloporphyrin-loaded SiO<sub>2</sub>. The results in **Fig 1** show that both the SiO<sub>2</sub> support and metalloporphyrin-loaded SiO<sub>2</sub> catalysts have irregular spherical structures. The

particle size and morphology of the SiO<sub>2</sub> support did not greatly change,<sup>[27]</sup> which showed the SiO<sub>2</sub> is relatively stable, and its structure was not damaged during metalloporphyrin immobilization.

Fourier-transform infrared spectroscopy (FT-IR) results are shown in **Fig 2 (A)**. The absorption peak at 3325 cm<sup>-1</sup> belongs to the pyridyl N-H stretching vibration in porphyrin, and the absorption peak at 968 cm<sup>-1</sup> was assigned to the pyridyl bending vibration in porphyrin. The peak from 2922 cm<sup>-1</sup> - 3117 cm<sup>-1</sup> was attributed to the C-H stretching vibration of porphyrin and pyrrole rings, and the peak at 1344 cm<sup>-1</sup> belonged to the pyridyl C=N stretching vibration in porphyrin. FePOP, MnPOP, FePOP-SiO<sub>2</sub>, and MnPOP-SiO<sub>2</sub> all have these characteristic absorption peaks.<sup>[28, 29]</sup> 3411 cm<sup>-1</sup> was the -OH vibrational absorption peak from the silicon support, while the peak at 1087 cm<sup>-1</sup> belonged to the Si-O vibration of the support. SiO<sub>2</sub>, PdPOP-SiO<sub>2</sub>, FePOP-SiO<sub>2</sub>, MnPOP-SiO<sub>2</sub>, and CoPOP-SiO<sub>2</sub> were all found to have these characteristic absorption peaks.<sup>[30]</sup> It can be concluded that the immobilized metalloporphyrin mimetic enzyme catalysts were successfully synthesized.

As shown in **Fig 2 (B)**, the first weight loss of immobilized metalloporphyrins and SiO<sub>2</sub> support that occurs near 373 K in the thermogravimetry (TG) curve is likely the loss of water adsorbed on the SiO<sub>2</sub> surface. The weight loss around 433 K - 473 K is attributed to the evaporation of DMF on the catalyst surface. Finally, the weight loss of chloropropyl functional silica, PdPOP-SiO<sub>2</sub>, FePOP-SiO<sub>2</sub>, MnPOP-SiO<sub>2</sub>, and CoPOP-SiO<sub>2</sub> from 708 K - 808 K were 2.18%, 6.21%, 13.28% 11.76%, and 11.88%, respectively. These weight losses are likely due to the weight loss of ionic liquids and the pyrolysis of metalloporphyrins on the catalyst surfaces. Moreover, the SiO<sub>2</sub> support has good thermal stability up to 1273 K,<sup>[31]</sup> and since the highest reaction temperature in this study was 393 K, it can assumed that the catalysts will have good

thermal stabilities in this study. Thus, temperature has no obvious effect on the catalyst structure during the experiment.

X-ray powder diffraction (XRD) patterns of the SiO<sub>2</sub> support, PdPOP-SiO<sub>2</sub>, FePOP-SiO<sub>2</sub>, MnPOP-SiO<sub>2</sub>, and CoPOP-SiO<sub>2</sub> are shown in Fig 2 (C). It was observed that the same characteristic diffraction peak appeared at 23° in all samples, and due to its broad shape, it can be inferred that it was the characteristic diffraction peak of amorphous SiO<sub>2</sub>.<sup>[32]</sup> The presence of this peak indicated that all samples have an SiO<sub>2</sub> metalloporphyrin skeleton which significantly degraded during not was immobilization. Moreover, the peak at 40° was the characteristic diffraction peak of the Pd(II) nanoparticles in the PdPOP-SiO<sub>2</sub> XRD patterns. In addition, the XRD patterns of immobilized metalloporphyrin catalysts showed characteristic diffraction peaks at 19°, 21°, and 26° which may be due to  $\pi$ - $\pi$  interactions between adjacent stacked porphyrins during metalloporphyrin immobilization.<sup>[33]</sup> Thus, the order and regularity of the molecular sieve pores were changed, which indicated that metalloporphyrins had been successfully loaded onto the SiO<sub>2</sub> support.

The immobilized palladiumporphyrin catalyst was also measured by X-ray photoelectron spectroscopy (XPS), and the results are shown in **Fig 2 (D)**. The peaks at 102.08 eV, 283.08 eV, 339.08 eV, 401.08 eV, and 531.08 eV were assigned to Si 2p, C 1s, Pd 3d, N 1s, and O 1s, respectively. These data demonstrate that the surface elements of the immobilized palladiumporphyrin were Si, C, Pd, N, and O.<sup>[34]</sup> This also indicated the successful synthesis of the immobilized palladiumporphyrin catalyst.

The physical adsorption isotherm and pore size distribution of SiO<sub>2</sub>, PdPOP-SiO<sub>2</sub>,

FePOP-SiO<sub>2</sub>, MnPOP-SiO<sub>2</sub>, and CoPOP-SiO<sub>2</sub> are shown in **Fig S1**, which showed that they are all typical mesoporous materials. The typical characteristics of mesoporous materials are an adsorption curve that is not consistent with the desorption curve belonging to an H<sub>1</sub>-type hysteresis loop.<sup>[35]</sup> In addition, according to the pore size distribution, the pore diameter of SiO<sub>2</sub>, PdPOP-SiO<sub>2</sub>, FePOP-SiO<sub>2</sub>, MnPOP-SiO<sub>2</sub>, and CoPOP-SiO<sub>2</sub> were 11.50 nm, 6.31 nm, 11.42 nm, 11.46 nm, and 7.60 nm, respectively. Hence, it can be concluded that immobilized metalloporphyrin catalysts were successfully synthesized. In addition, the Brunner–Emmet–Teller (BET) measurements data of specific surface area, pore volume, and pore size are also shown in **Table 1**. According to this data, the chemical modification of the surface of the porous materials appears to affect their surface properties. The surface area, pore volume, and pore size of immobilized metalloporphyrins were all lower compared with the SiO<sub>2</sub> support, likely due to the loading of ionic liquids and metalloporphyrins on the surface of SiO<sub>2</sub>.

Organic and metal elements of the catalysts are shown in **Table S1**. The content of C, H, and N of the unmodified SiO<sub>2</sub> and chloropropyl-functionalized silica were analyzed, which showed that 0.56 mmol·g<sup>-1</sup> of the silane modifier was loaded onto SiO<sub>2</sub>.<sup>[36]</sup> The amount of C, H, N, and metal elements of immobilized metalloporphyrin catalysts were also analyzed. The results showed that the loading of metalloporphyrin of PdPOP-SiO<sub>2</sub>, FePOP-SiO<sub>2</sub>, MnPOP-SiO<sub>2</sub>, and CoPOP-SiO<sub>2</sub> were 0.49 mmol·g<sup>-1</sup>, 0.02 mmol·g<sup>-1</sup>, 0.66 × 10<sup>-3</sup> mmol·g<sup>-1</sup>, and 0.13 mmol·g<sup>-1</sup>, respectively.<sup>[37]</sup> The PdPOP-SiO<sub>2</sub> catalyst contained the highest amount of metalloporphyrin loaded onto the SiO<sub>2</sub> support.

#### 3.2. Comparison of catalytic activity of different biomimetic oxidase

To identify the best biomimetic oxidase for HMF oxidation, a series of

experiments were carried out to catalyze HMF oxidation with different catalysts. The catalytic activities of the SiO<sub>2</sub> carrier and no catalyst under the same reaction conditions are shown in **Table 1**, entries 6-7. When heated for 12 h at 363 K without catalyst, small amount of HMF was oxidized and decomposed in the control group. The experimental results in **Table 1** showed that the catalytic activity of immobilized palladiumporphyrin was much better than that of the other catalysts. The HMF conversion and FDCA yield using the palladiumporphyrin catalyst were 48.98% and 38.91%, respectively. Moreover, the pore size, pore volume, and specific surface area of the palladiumporphyrin catalyst in Table 1 are the smallest among the metalloporphyrin catalysts. highest This indicates that the amount of metalloporphyrin was loaded onto SiO<sub>2</sub> support in the PdPOP-SiO<sub>2</sub> catalyst, according to **Table S1**. Moreover, PdPOP-SiO<sub>2</sub> is not prone to  $\pi$ - $\pi$  stacking which prevented auto-oxidation and deactivation of catalytic center. Hence, it can be inferred that the surface modification of the support and the successful grafting of metalloporphyrins gave the immobilized palladiumporphyrin catalyst ideal catalytic activity. Thus, immobilized palladiumporphyrin catalysts were selected for further HMF oxidation studies.

#### 3.3 Effect of different solvents on HMF oxidation

Solvents play very important roles during chemical reactions due to different polarities, conductivities, dielectric constants, and pH values.<sup>[38]</sup> To determine the best solvent for HMF oxidation, a series of experiments were carried out in various solvents, such as ethanol, toluene, acetonitrile, water, and dimethyl sulfoxide, and the results are summarized in **Fig 3.** Water was the best solvent for HMF oxidation, since the HMF conversion and FDCA yield were 75.44% and 76.26%, respectively. These results may be due to the high polarity of water. The polarity of toluene, ethanol, acetonitrile,

dimethyl sulfoxide, and water are 2.4, 6.0, 6.2, 7.2, and 10.2, respectively. According to the principle of similar phase dissolution, since the polarity of the substrate HMF and product FDCA were also relatively high, water was the optimal solvent to dissolve the reaction substrate and products. The polarities of ethanol and toluene are relatively low, and the product FDCA is insoluble in the reaction system, which explains why the FDCA yield in ethanol and toluene were only 0.97% and 1.23%, respectively. Relatively higher HMF conversions of 37.78% and 49.17% and FDCA yields of 21.04% and 45.33% in acetonitrile and dimethyl sulfoxide were obtained, respectively, which are lower than those of water. These differences may be because water is the most polar solvent, and the dispersion of catalyst in organic solvents is not good, which reduces catalytic activity. Thus, water was the best reaction solvent and is both cheap and environmentally-friendly.

#### 3.4. Effect of catalyst dosage on HMF oxidation

In this study, different catalyst amounts were used to determine the effect of dosage on HMF oxidation. A series of experiments were carried out with 20 mg, 40 mg, 60 mg, 80 mg, and 100 mg catalyst. In **Fig 4**, the HMF conversion and FDCA yield initially increased as the catalyst amount increased. For example, 64.14% and 100% HMF conversion were acquired after 12 h reaction using 20 mg and 80 mg of catalyst, and the corresponding FDCA yields were 61.22% and 90.48%. This increase was attributed to an increase in the number of catalytic active sites as the catalyst amount increased. Further increasing the catalyst amount did not change the HMF conversion and FDCA yield they were in equilibrium.<sup>[39]</sup> This may be due to the saturated adsorption of HMF substrate onto the catalyst active sites, which effectively reduced the amount of catalyst available to convert substrate into product. However, when the catalyst amount reached to 100 mg, we found that nearly 10% compounds

was not detected. Since the temperature and base dosage were not high, the substrate should not have been degraded. Thus, it is likely that products were absorbed onto the catalyst so that a portion of the products were not detected. When the catalyst was ultrasonicated for 20 min, 5.72% FFCA and 0.38% FDCA were obtained. Therefore, to ensure sufficient catalytic active sites in the reaction system to catalyze the oxidation of HMF and the catalysts did not seriously adsorb the products. Thus, 80 mg of catalyst was selected for the next experiment.

#### 3.5 Effect of base and oxidant on HMF oxidation

Base played an important role in HMF oxidation into FDCA since bases can neutralize the FDCA and prevent it from being adsorbed onto the catalyst surface.<sup>[40]</sup> Therefore, we explored the optimum amount of base in the HMF oxidation system, and the results in **Table 2** show that HMF conversion (33.06%) and FDCA yield (14.24%) were relatively low without base. Further increasing the amount of base increased both the HMF conversion and FDCA yield, but when the base amount was increased to 6 mg, a side reaction occurred. It is proposed that high base concentrations degrade the HMF, thus 4 mg base was selected for the next experiment. The oxidizing effects of tert-butylhydroperoxide and oxygen were compared, and it was found that oxygen was better. Since oxygen is a green oxidant, it is potentially a better choice due to its abundant resources and lack of toxic pollution.

#### 3.6. Effects of temperature on HMF Oxidation

Experiments were performed at different temperatures from 313 K to 393 K, and the results in **Fig 5** show that temperature had an important effect on HMF conversion and FDCA yield. Generally speaking, HMF conversion and FDCA yield were improved as the reaction temperature increased. At 313 K, the HMF conversion and FDCA yields were 69.08% and 62.41%, respectively. When the reaction temperature

was increased to 333 K, 353 K, and 373 K, HMF conversions were 82.81%, 91.15%, and 100%, and FDCA yields were 74.06%, 82.38%, and 92.94%, respectively. However, when the temperature was further increased to 393 K, the FDCA yield was 91.40%, and no other intermediate product was detected. At 393 K, the temperature was likely too high, and the HMF substrate was degraded into other by-products.<sup>[41]</sup> Therefore, 373 K was selected for the following experiment.

#### **3.7 Effect of time course on HMF conversion**

To study optimal HMF oxidation reaction time using PdPOP-SiO<sub>2</sub>, different time points were recorded during the oxidation reaction, and the results are shown in **Fig 6**. The HMF conversion and FDCA yield gradually increased during the oxidation process,<sup>[42]</sup> and complete HMF conversion was achieved between 8 h and 12 h. The FDCA yield also gradually increased at longer reaction times, and the FDCA yield was 97.34% after 24 h. However, the FDCA yield reached equilibrium at 12 h with a yield of 94.94%.

#### 3.8 Kinetics of HMF oxidation via biomimetic oxidase catalyst

The reaction kinetics model was established based on the catalyst concentration and reaction temperature (E-supplementary data). A reaction mechanism model for the catalytic oxidation of HMF by immobilized metal palladium porphyrin was proposed (**Fig. S2**). The kinetic reaction constants are shown in **Table 3**, where  $K_1$  and  $K_3$ represent the oxidation of the aldehyde group,  $K_2$  represents the oxidation of the hydroxyl group. The oxidation experiment was conducted at 343 K, 353 K, and 363 K, and the catalyst dosage was 40 mg, 60 mg, or 80 mg. It was demonstrated from **Table 3** that the rate constants were in the order  $K_1 > K_2 > K_3$  in the reaction route HMF $\rightarrow$ HFCA $\rightarrow$ FFCA $\rightarrow$ FDCA, indicating the oxidation of FFCA to FDCA was the rate-limiting step. A possible explanation is that electrons in the furan were attracted to

HFCA to form a carboxyl group during the oxidation of HMF, which generated an unstable free radical with a resonance structure during the formation of FDCA<sup>[43]</sup>. **Table 3** shows that the reaction rate constant increased as both the temperature and catalyst dosage increased.

#### **3.9. Reusability test of catalyst**

To verify the reusability of the heterogeneous catalysts, recycling experiments of PdPOP-SiO<sub>2</sub> were carried out at 373 K with 80 mg catalyst for 12 h. After the reaction, the supernatant was discarded, and the recycled catalyst was washed with deionized water twice and then dried at 353 K for the next cycle. The results in **Fig 7** show that after the catalysts were reused for 5 cycles, the HMF conversion was still 100%, and the FDCA yield was slightly reduced from 94.94% to 93.13%. The experimental results showed that the repeatability of the catalyst was remarkable, and the catalyst can be reused.

#### 4. Conclusion

In summary, the PdPOP-SiO<sub>2</sub>, MnPOP-SiO<sub>2</sub>, FePOP-SiO<sub>2</sub>, and CoPOP-SiO<sub>2</sub> catalysts were successfully prepared via covalent binding of metalloporphyrin nanoparticles onto the functioned surface of mesoporous SiO<sub>2</sub> and characterized by SEM, XRD, TG, FT-IR, XPS, and BET techniques. The PdPOP-SiO<sub>2</sub> catalyst demonstrated the highest catalytic activity during HMF oxidation into FDCA using mild reaction conditions. The metal active center of the catalyst was critical for HMF oxidation. In addition, the solvent, catalyst amount, base dosage, oxidant, temperature, and reaction time also showed significant effects on HMF conversion and FDCA selectivity. Under optimum reaction conditions, 100% HMF conversion and 94.94% FDCA yield were archived after 12 h reaction at 373 K, using PdPOP-SiO<sub>2</sub> as the catalyst. Compared with previously-reported, the our catalytic system shows the

following notable advantages: (a) PdPOP-SiO<sub>2</sub> catalyst avoids the need for high base concentrations; (b) the reaction could be carried out under atmosphere, and does not require high oxygen pressure; (c) biomimetic oxidase PdPOP-SiO<sub>2</sub> could be simply separated from the reaction system and further recycled without severe loss of activity; (d) water was the optimal reaction solvent for HMF conversion and is both cheap and environmentally-friendly. Therefore, biomimetic oxidase developed in this study has promising potential for large-scale FDCA production for use in renewable biomass-based platform chemicals.

#### **5.** Conflict of interest

The authors declare no conflict of interest.

#### Acknowledgments

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#### **Figure and table captions:**

**Scheme 1** Reaction pathway from 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA).

Scheme 2 Immobilization process of metalloporphyrins onto ionic liquid modified mesoporous SiO<sub>2</sub>.

**Fig 1.** SEM images of (a) SiO<sub>2</sub>, (b) CoPOP-SiO<sub>2</sub>, (c) MnPOP-SiO<sub>2</sub>, (d) FePOP-SiO<sub>2</sub>, (e) PdPOP-SiO<sub>2</sub>(5000 multiple), (f) PdPOP-SiO<sub>2</sub>(500 multiple).

**Fig 2.** FT-IR spectra(A), TG spectra(B), XRD patterns(C) and XPS spectra (D) of immobilized biomimetic oxidase.

**Fig 3**. Effect of the solvents on the HMF oxidation. (Reaction conditions: PdPOP-SiO<sub>2</sub> (60 mg), HMF (10 mg), 373 K, 12 h.)

**Fig 4**. The effect of catalyst dosage on the HMF oxidation. (Reaction conditions: Solvent: H<sub>2</sub>O, HMF (10 mg), 373 K, 12 h.)

**Fig 5**. The effect of reaction temperature on the HMF oxidation. (Reaction conditions: PdPOP-SiO<sub>2</sub> (80 mg), Solvent: H<sub>2</sub>O, HMF (10 mg), 12 h.)

**Fig 6**. Effect of the reaction time on the HMF oxidation. (Reaction conditions: PdPOP-SiO<sub>2</sub> (80 mg), HMF (10 mg), Solvent: H<sub>2</sub>O, 373 K.)

**Fig 7**. Recycle experiments of the biomimetic oxidase. (Reaction conditions: PdPOP-SiO<sub>2</sub> (80 mg), HMF (10 mg), Solvent: H<sub>2</sub>O, 373 K, 12 h.)



Fig. 1







Fig. 3



Fig. 4



Fig. 5



Fig. 6



Fig. 7

O Terephthalic acid (TPA) ∬ from fossil oil HQ *\_*0 HC ò 5-hydroxymethylfurfural (HMF) from biomass OH ) O C 0 \_\_O Replace Ò HO HO óн ЮH 5-formyl-2-furancarboxylic acid(FFCA) 2,5-furandicarboxylic acid(FDCA) 5-hydroxymethyl-2-furancarboxylic acid(HFCA)

Scheme1

![](_page_31_Figure_1.jpeg)

Scheme 2

### **Table captions**

- **Table 1.** Catalytic activity and BET data of various biomimetic oxidase.
- **Table 2.** The effect of base dosage and oxidant type on the HMF oxidation..
- **Table 3** The effect of biomimetic oxidase dosage and temperature on reaction rate.

# 

Entry	Biomimetic oxidase	HMF conversion (%)	FDCA yield (%)	HFCA yield (%)	FFCA yield (%)	Surface aera (m²/g)	Pore volume	Pore diameter
1	CoPOP-SiO <sub>2</sub> <sup>a</sup>	25.84	8.52	5.04	0.23	171	0.42	7.60
2	FePOP-SiO <sub>2</sub> <sup>a</sup>	23.66	7.59	4.56	0.41	173	0.48	11.42
3	MnPOP-SiO <sub>2</sub> <sup>a</sup>	19.43	0.29	0.57	0.59	185	0.55	11.46
4	PdPOP-SiO <sub>2</sub> <sup>a</sup>	48.98	38.91	2.46	9.65	171	0.41	6.31
5	PdPOP-SiO <sub>2</sub> <sup>b</sup>	69.08	62.41	4.81	1.32	171	0.41	6.31
6	SiO <sub>2</sub> <sup>c</sup>	4.1	-	0.23	2.13	213	0.61	11.50
7	No oxidase <sup>d</sup>	3.4	-	1.21	1.52	-		-

Table 1. Catalytic activity and BET data of various biomimetic oxidase.

<sup>a</sup> Reaction conditions: HMF (10 mg), oxidase (50 mg), H<sub>2</sub>O (4 g), TBHP (64.45 mg), NaOH (4 mg), 363 K, 12 h. <sup>b</sup> Reaction conditions: HMF (10 mg), oxidase (80 mg), H<sub>2</sub>O (4 g), O<sub>2</sub>, NaOH (4 mg), 313 K, 12 h.

 $^{\rm c}$  Reaction conditions: HMF (10 mg), SiO<sub>2</sub> (50 mg), H<sub>2</sub>O (4 g) , TBHP (64.45 mg), NaOH (4 mg) , 363 K, 12 h. <sup>d</sup> Reaction conditions: HMF (10 mg), no oxidase, H<sub>2</sub>O (4 g), TBHP (64.45 mg), NaOH (4 mg), 363 K, 12 h.

#### D ۰

Entry	Base dosage	HMF conversion	FDCA yield	HFCA yield	FFCA yield
1	0 mg <sup>a</sup>	33.06	14.24	10.84	3.42
2	2 mg <sup>a</sup>	100	82.87	-	16.90
3	4 mg <sup>a</sup>	100	94.94	-	5.68
4	6 mg <sup>a</sup>	100	49.16	-	14.21
5	4 mg <sup>b</sup>	68	47.23	2.34	17.35

Table 2. The effect of base dosage and oxidant type on HMF conversion.

<sup>a</sup> Reaction conditions: HMF (10 mg), Oxidase: PdPOP-SiO<sub>2</sub> (80 mg), H<sub>2</sub>O (4 g), O<sub>2</sub>, 373 K, 12 h. <sup>b</sup> Reaction conditions: HMF (10 mg), Oxidase: PdPOP-SiO<sub>2</sub> (80 mg), H<sub>2</sub>O (4 g), TBHP (64.45 mg), 373 K, 12 h.

	Condition	$K_1$ (h <sup>-1</sup> )	$K_2$ (h <sup>-1</sup> )	$K_3$ (h <sup>-1</sup> )
	343	0.12	0.10	0.04
Temperature (K)	353	0.14	0.13	0.06
	363	0.17	0.16	0.08
	40	0.15	0.14	0.04
Oxidase dosage	60	0.17	0.16	0.08
(mg)	80	0.18	0.17	0.09

Table 3	The e	effect of	biomimetio	c oxidase	dosage and	temperature	on reaction rate