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A novel magnetic palladium catalyst for the mild aerobic oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid in water

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In this study, magnetically separable, graphene oxide-supported palladium nanoparticles (C-Fe₃O₄-Pd) were successfully prepared *via* a one-step solvothermal route. The C-Fe₃O₄-Pd catalyst showed excellent catalytic performance in the aerobic oxidation of 5-hydroxymethylfurfural (HMF) into 2,5-furandicarboxylic acid (FDCA). The base concentration and reaction temperature significantly affected both HMF conversion and FDCA selectivity. High HMF conversion (98.2%) and FDCA yield (91.8%) were obtained after 4 h at 80 °C with a K₂CO₃/HMF molar ratio of 0.5. The C-Fe₃O₄-Pd catalyst was easily collected by an external magnet and reused without significant loss of its catalytic activity. The developed method is a green and sustainable process for the production of valuable FDCA from renewable, bio-based HMF in terms of the use of water as solvent, the use of stoichiometric amount of base, high catalytic activity under atmospheric oxygen pressure, and facile recyclability of the catalyst.

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Introduction

Currently, there is a growing concern stemming from the gradual depletion of fossil oil reservoirs and the awareness of climate change.^{1,2} Much effort has been devoted to the search for renewable resources as alternatives to fossil resources in supplying chemicals and fuels. Biomass, which is the only carbon-containing renewable resource, consists mainly of carbohydrate components such as starch, cellulose, and hemicellulose. It is not only abundant on the earth, but also keeps the carbon balance. Through biorefinery, biomass can be converted into useful chemicals and valuable fuel.^{3–5}

Among a range of potential platform compounds, 5-hydroxymethylfurfural (HMF) can be generated by acidcatalyzed dehydration of C6-sugar monomers.^{6–9} It has been identified as a versatile platform chemical with high potential for the synthesis of valuable chemicals and liquid fuels.¹⁰ Recently, selective oxidation of HMF has been of particular interest, since it can produce several important chemicals, such as 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) and 2,5-furandicarboxylic acid (FDCA) (Scheme 1).^{11–13} FDCA has been identified as one of the top 12 value-added chemicals from biomass by the U.S. Department of Energy. It has a similar structure with terephthalic acid; thus it has high potential as a substitute for terephthalic acid in the manufacture of poly(ethylene terephthalate) (PET) plastics.¹⁴ Therefore, there is growing attention on the synthesis of FDCA by the oxidation of HMF.

The oxidation of HMF into FDCA has been performed under different reaction conditions using both homogeneous and heterogeneous catalysts. In an early work, the combined $Co^{2+}/Mn^{2+}/Br^{-}$ catalysts were used for the oxidation of HMF into FDCA in acetic acid at 125 °C under 70 bar air pressure.¹⁵ As it is difficult to recycle homogeneous catalysts, researchers mainly focused on the development of new heterogeneous catalysts for the oxidation of HMF into FDCA. In most cases, inorganic material-supported Pt, Pd, Ru and Au nanoparticles have been used as heterogeneous catalysts for the aerobic oxidation of HMF into FDCA. For example, Davis et al. reported that Pd/C and Pt/C catalysts promoted the full oxidation of HMF, with FDCA yields between 71% and 79% and NaOH/HMF mole ratio of 2 under 690 kPa O2 pressure.¹⁶ Supported Au nanoparticles have shown encouraging catalytic performance for the aerobic oxidation of HMF



Scheme 1 Major oxidation products from the oxidation of HMF.

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Paper

to FDCA in water and have received great interest.^{17–21} However, the stability of the supported Au catalysts in the aerobic oxidation of HMF remains a problem. For example, Corma *et al.* reported that CeO₂-supported Au nanoparticles (CeO₂/ Au) showed high catalytic activity for the oxidation of HMF to FDCA with a high yield of 99% at 130 °C under 1 MPa air pressure and high concentration of NaOH (4 equiv of HMF), but the activity of CeO₂/Au in the second run declined sharply.¹⁷ In addition, most of the currently reported methods require the use of high amounts of base (with 2–20 mole ratio of HMF) and high oxygen pressure. Acknowledging these important achievements, the quest for milder and greener methodologies for selective oxidation of HMF into FDCA still remains a great challenge.

In recent years, graphene-based materials such as graphene and graphene oxide (GO) have shown important applications in various fields such as electrochemistry, electronics, biochemistry, and hydrogen storage.²² Graphene-based materials have also received extensive attention as a promising support to stabilize nanoparticles, including metals and metal oxides, by strong π -interactions between the nanoparticles and the supporting carbon nanosheets.²³ Among them, graphene oxide–Fe₃O₄ nanoparticles, which are formed by the decoration of Fe₃O₄ on the graphene oxide, have particularly been attractive as an excellent carbonaceous support in catalyst and separation fields due to their facile recovery using an external magnet.²⁴

Recently, the use of palladium nanoparticles has attracted strong interest owing to their high catalytic activity compared to the bulk phase.²⁵ In order to prevent the aggregation of palladium nanoparticles, several kinds of supports have been used to immobilize the palladium nanoparticles. However, the recyclability of supported palladium nanoparticles suffers from the need for cost- and time-intensive filtration methods. One effective method to solve this problem is the application of magnetic supports, which allow the recovery of Pd nanoparticles by simple decantation in the presence of an external magnet.^{26,27} In an attempt to develop a green and sustainable method for the oxidation of HMF into FDCA under mild conditions, we used the abovementioned graphene-magnetite nanocomposite as a supporting material for the immobilization of palladium nanoparticles, which can act as a magnetically separable catalyst for the oxidation of HMF into FDCA.

Experimental section

Materials

Ethylene glycol (99.5%), FeCl₃·6H₂O (99.5%), sodium acetate (NaOAc, 99.5%), NaOH (99.5%), NaNO₃ (99.5%) and KMnO₄ (99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). HCl (36.5%) and H₂SO₄ (98.0%) were purchased from Kaifeng Chemical Reagent Co., Ltd. (Kaifeng, China). Graphite powder and sodium tetrachloropalladate(π) (Na₂PdCl₄, 98%) were purchased from Aladdin Chemicals Co. Ltd. (Beijing, China). HMF (98%) was purchased from Beijing Chemicals Co. Ltd. (Beijing, China).

DFF (98%) and FDCA (97.0%) were purchased from the J&K Chemical Co. Ltd., (Beijing, China). Acetonitrile (HPLC grade) was purchased from Tedia Co. (Fairfield, USA). All the solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Preparation of graphite oxide

Graphite oxide was prepared by a modified Hummer's method.²⁸ Graphite (3.0 g) and NaNO₃ (2.25 g) were added into a 1000 mL beaker in an ice bath. Then, 98.0 wt.% H₂SO₄ (225 mL) was added into the beaker and vigorously stirred for 30 min. Then, KMnO₄ (13.5 g) was added into the mixture slowly over 2 h. After the addition of KMnO₄, the mixture was stirred for 2 h at 0 °C and subsequently at 25 °C for 5 days. After that, the temperature was raised to 98 °C, and 5 wt.% H₂SO₄ (450 mL) was added dropwise over 1 h. Then, the mixture was stirred to 25 °C, and the mixture was stirred for another 2 h. Finally, the solid product was collected by centrifugation and washed 15 times with 3 wt.% H₂SO₄, followed by washing 5 times with 3 wt.% HCl. Finally, the solid product was dried in a vacuum oven at 40 °C to obtain graphite oxide.

Synthesis of C-Fe₃O₄-Pd composite

30 mg of graphite oxide was added to 10 mL of water, and the mixture was subjected to sonication for 30 min in order to homogeneously disperse graphite oxide into water. 20 mL of ethylene glycol was then added to the above mixture, followed by sonication for additional 30 min. Then, FeCl₃·6H₂O (0.1 g) and NaOAc (1.2 g) were added to a mixed solvent of water (5 mL) and ethylene glycol (10 mL); then the mixture was stirred at room temperature for 1 h to obtain a clear solution. The as-prepared clear solution was added dropwise to the graphite oxide solution, and then the mixture was stirred for 30 min. Then, Na₂PdCl₄ (4 mg) dissolved in 5 mL of N,N-dimethylformamide was added dropwise, and the mixture was stirred for another 30 min. Finally, the mixture was transferred into an autoclave and kept still at 130 °C for 14 h. After cooling to room temperature, the catalyst was collected by an external magnet, washed with water and ethanol, and dried in a vacuum oven at 40 °C. Finally, 37 mg of the black catalyst was obtained, which was abbreviated as C-Fe₃O₄-Pd.

Catalyst characterization

Transmission electron microscope (TEM) images were obtained using an FEI Tecnai G²-20 instrument. The sample powder was firstly dispersed in ethanol and dropped onto copper grids for observation. X-ray powder diffraction (XRD) patterns of samples were determined with a Bruker advanced D8 powder diffractometer (Cu K α). All XRD patterns were collected in the 2 θ range of 10–80° with a scanning rate of 0.016° s⁻¹. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo VG scientific ESCA MultiLab-2000 spectrometer with a monochromatized Al K α source (1486.6 eV) at constant analyzer pass energy of 25 eV. The binding energy was estimated to be accurate within 0.2 eV. All binding energies (BEs) were corrected referencing the C 1s (284.6 eV) peak of the contamination carbon as an internal standard. FT-IR measurements were recorded on a Nicolet NEXUS-6700 FTIR spectrometer with a spectral resolution of 4 cm⁻¹ in the wave number range of 500–4000 cm⁻¹. The Pd content in the C–Fe₃O₄–Pd catalyst was quantitatively determined by inductively coupled atomic emission spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). Magnetization measurement was performed by using a physical property measurement system (PPMS-9T) with VSM option from Quantum Design. Applied magnetic fields H between –30 and 30 kOe and temperature 300 K were used in the experiments.

Determination of Pd loading by ICP-AES

The palladium content in the C–Fe₃O₄–Pd catalyst was quantitatively determined by inductively coupled atomic emission spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). The acid digestion solution was composed of concentrated HNO₃ (7.5 mL), 48 wt.% HF (1.5 mL) and 2.5 mL concentrated HCl (2.5 mL). 0.5 g sample was digested in the above solution on the flat electric furnace. After digestion, the sample was diluted with deionized water and centrifuged at 3000 rpm. The supernatant liquid was subjected to ICP-AES analysis. The ICP-AES operation conditions were as follows: incident power: 1.1 KW, carrier gas flow rate: 0.8 L min⁻¹, auxiliary gas flow rate: 0.4 L min⁻¹, coolant gas flow rate: 16 L min⁻¹, observation height: 10 mm.

General procedure for the aerobic oxidation of HMF

Typically, HMF (50.4 mg, 0.4 mmol) was firstly dissolved in water (8 mL); then K_2CO_3 (27.6 mg, 0.2 mmol) and C–Fe₃O₄–Pd (40 mg, Pd/HMF mol ratio = 1.8%) were added to the above reaction solution. Then oxygen was flushed at a rate of 20 mL min⁻¹, and the reaction was carried out at 80 °C with stirring at a constant rate of 600 revolutions per minute (rpm) using a condenser. After the reaction, the catalyst was removed, and the reaction solution was diluted with water to a certain volume in each case.

Analytic methods

Furan compounds were analyzed by a ProStar 210 HPLC system equipped with a UV detector. Furan compounds were well separated by a reversed-phase C18 column (200×4.6 mm) at the wavelength of 280 nm. Acetonitrile and 0.1 wt.% acetic acid aqueous solution with a volume ratio of 30:70 were used as mobile phase at a flow rate of 1.0 mL min⁻¹. The amounts of HMF and FDCA in samples were obtained directly by interpolation from calibration curves. HMF conversion and FDCA yield are defined as follows:

HMF conversion = moles of HMF/moles of starting HMF \times 100%

FDCA yield = moles of FDCA/moles of starting HMF \times 100%

Catalyst recycling

After the reaction, the C–Fe₃O₄–Pd catalyst was collected using a permanent magnet, and the liquid solution was decanted. Then, the spent catalyst was washed with water three times and ethanol twice. Finally, it was dried under vacuum at 50 °C overnight. The spent catalyst was reused for the next run, and the other steps remained the same.

Results and discussion

Catalyst preparation and characterization

Scheme 2 shows the procedure for the preparation of the C-Fe₃O₄-Pd catalyst. Firstly, graphite oxide was prepared by the oxidation of pristine graphite by a modified Hummer's method. Both Pd²⁺ and Fe³⁺ ions were then simultaneously anchored on the surface of graphene oxide by π -bonding²⁹ or ionic interaction between the oxy functional groups of graphene oxide and the corresponding positive charge of the metal ions.³⁰ Then, the metal cations immobilized on graphene oxide were solvothermally reduced to graphene-Fe₃O₄-Pd nanocomposite by ethylene glycol at 130 °C for 14 h.³¹ The C-Fe₃O₄-Pd catalyst was readily purified using an external magnet. The Pd content was determined to be 1.95 wt.% by ICP-AES analysis, which meant 1 g of the catalyst contained 19.5 mg of Pd.

The heterostructure of the C–Fe₃O₄–Pd catalyst can be verified by the morphological analyses. Fig. 1 shows the typical TEM images of graphite oxide and the C–Fe₃O₄–Pd catalyst. In Fig. 1(a), the folding nature of graphite oxide is clearly visible. On the other hand, graphene oxide has a layer structure, which is believed to be composed of many individual sheets.³² As shown in Fig. 1(b), the surface of graphene oxide is decorated by the palladium and Fe₃O₄ nanoparticles, and almost no particles are scattered out of the supports, which indicates that there was a strong interaction between nanoparticles and the support.²⁹ The morphologies of those nanoparticles



Scheme 2 Schematic illustration of the catalyst preparation.



Fig. 1 TEM images of graphite oxide (a) and C-Fe₃O₄-Pd (b).

are almost regular in nature, and most of them are quite spherical, with an average diameter of 10 nm. In addition, as the density and color of Fe_3O_4 are close to those of Pd nanoparticles, it was difficult to discriminate Fe_3O_4 and Pd nanoparticles in the C-Fe₃O₄-Pd catalyst. The C-Fe₃O₄-Pd catalyst was well dispersed in water, similar to that reported by Yu *et al.*,³³ which is beneficial to the contact between the substrate and the catalyst sites for chemical reactions in water.

XRD patterns of the graphite and the C-Fe₃O₄-Pd catalyst are shown in Fig. 2. A strong XRD peak at $2\theta = 26.4^{\circ}$ was observed in graphite (Fig. 2(a)), which is the characteristic XRD peak of graphite and can be assigned to hexagonal



Fig. 2 XRD diffraction patterns of (a) graphite and (b) the C–Fe $_3O_4$ –Pd catalyst.

crystalline graphite (JCPDS no. 41-1487).^{34,35} As shown in Fig. 2(b), after chemical oxidation of graphite by KMnO₄, the strong peak at $2\theta = 26.4^{\circ}$ disappeared in the spectrum of the C-Fe₃O₄-Pd catalyst, revealing the successful oxidation of the starting graphite.³⁰ However, no obvious diffraction peaks of graphite oxide were observed in the XRD patterns of the C-Fe₃O₄-Pd catalyst. It is reported that when the regular stacks of graphite oxide were destroyed, for example, by exfoliation, their diffraction peaks disappeared.³⁶ The diffraction peaks at $2\theta = 30.1^{\circ}$, 35.4° , 43.1° , 56.9° , and 63.2° were assigned to the reflections of Fe₃O₄, which matched well with the standards of Fe₃O₄ (JCPDS 65–3107).³⁷ In addition, the peak at 2θ = 40.1° is also clearly observed, which is attributed to the interplanar spacing for the (111) plane of Pd(0) nanoparticles.³³ From the XRD results, it is confirmed that Fe_3O_4 and Pd(0)nanoparticles were successfully immobilized on the surface of the graphene oxide.

FT-IR is one of the most important methods to study the oxidation of graphite to graphite oxide. Fig. 3 shows the FT-IR spectrum of the C–Fe₃O₄–Pd catalyst. As shown in Fig. 3, several functional groups appeared after the chemical oxidation of graphite, such as –OH (3396 cm⁻¹), –COOH (1725 cm⁻¹), C–O (1058 cm⁻¹) and C=O (1622 cm⁻¹). These functional groups clearly indicate that the graphite was successfully oxidized by KMnO₄. The functional groups in graphene oxide have a strong tendency to interact with metal cations, with its enhanced hydroxyl and carboxyl groups. In addition, a peak at 582 cm⁻¹ was also observed, which is assigned to Fe–O vibrations of Fe₃O₄.³⁴

The XPS survey scan spectra of the C-Fe₃O₄-Pd catalyst and Pd 3d region is shown in Fig. 4. These peaks, with a binding energy of about 285, 531, and 711 eV, are attributed to C 1s, O 1s, and Fe 2p, respectively (Fig. 4(a)). In addition, a weak peak with the centre around 335 eV was also observed, which was assigned to Pd 3d. In the case of Fe 2p, two peaks of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ are located at 711.9 and 725.3 eV, respectively, which are the characteristic XPS peaks of Fe²⁺ in Fe₃O₄.³⁸ In order to give clear information on Pd valence, high-resolution XPS spectra of Pd 3d was also collected (Fig. 4(b)). The binding energy of Pd 3d_{3/2} and Pd 3d_{5/2}



Fig. 3 FT-IR spectra of the C-Fe₃O₄-Pd catalyst.



Fig. 4 XPS spectra of the samples: (a) survey scan of the C–Fe $_3O_4$ –Pd catalyst, (b) Pd 3d region.

were 335.2 eV and 340.4 eV, respectively. The two peaks are the characteristic peaks of Pd(0), which is in agreement with the previous report,³⁹ suggesting that the absorbed Pd(π) in the graphene oxide was successfully reduced to Pd(0) nanoparticles under solvothermal reduction. Taking the XPS results together with XRD information into consideration, Fe₃O₄ and Pd(0) were successfully decorated on the surface of graphene oxide.

A magnetic catalyst should possess sufficient paramagnetic properties for practical applications. Therefore, vibrating sample magnetometer (VSM) analysis was used to test the magnetic property of the C–Fe₃O₄–Pd catalyst, and its magnetic curve is shown in Fig. 5. The isothermal magnetization curve of the C–Fe₃O₄–Pd catalyst at 300 K with the field sweeping from $-30\,000$ to $+30\,000$ Oe displayed a rapid increase with increasing applied magnetic field due to superparamagnetic relaxation. The saturation magnetization was 28.75 emu g⁻¹. Therefore, the magnetization of C–Fe₃O₄–Pd





catalyst is strong enough for magnetic separation by a permanent magnet, as shown in Fig. 6.

Aerobic oxidation of HMF over C-Fe₃O₄-Pd catalyst in various solvents

In previous reports, some methods used organic solvents for the oxidation of alcohols using Pd-based catalysts,⁴⁰ while others used water as the solvent for the oxidation of alcohols.⁴¹ Those reports indicated that the solvent played a crucial role in the chemical reactions. Indeed, different solvents have different properties, such as polarity, dielectric constant, steric hindrance, and pH, which affect the efficiency of chemical reactions.⁴² In addition, it is reported that the supported metal nanoparticles may be deactivated by the formed organic products, such as carboxylic acid. Thus, a base is usually required to quickly neutralize the produced carboxylic acid and keep the catalyst active.43 Therefore, the oxidation of HMF over C-Fe₃O₄-Pd catalyst was initially carried out in some common solvents using 0.5 equiv of K₂CO₃ as additive. As shown in Table 1, the reaction solvent greatly affected both HMF conversion and product selectivity. Generally speaking, HMF conversion and the total selectivity of the furan products were higher in polar solvents than those obtained in solvents with low polarity, such as toluene and MIBK. One of the main reasons should be that the base K₂CO₃ and the product FDCA showed poor solubility in toluene and MIBK. Thus, the formed FDCA could not be quickly



Fig. 6 Simple separation of the catalyst by a magnet: (a) after reaction, (b) after separation by an external magnet.

Paper

 Table 1
 Results of the aerobic oxidation of HMF in different solvents^a

| Entry | Solvent | HMF con. (%) | FDCA yield (%) | DFF yield (%) | HMFCA yield (%) | Total sel. of furans $(\%)^d$ |
|----------------|---------|--------------|----------------|---------------|-----------------|-------------------------------|
| 1 | Toluene | 9.2 | 2.0 | 3.5 | 0.9 | 75.0 |
| 2 | MIBK | 21.9 | 16.2 | 2.3 | 0.4 | 86.3 |
| 3 | DMSO | 50.6 | 0 | 30.0 | 14.1 | 87.2 |
| 4^b | DMSO | 52.7 | 45.8 | 1.4 | 0.9 | 91.3 |
| 5 | Ethanol | 61.2 | 50.4 | 3.8 | 1.2 | 90.5 |
| 6 | H_2O | 87.2 | 82.3 | 1.2 | 0.9 | 96.8 |
| 7 ^c | H_2O | 12.1 | 11.1 | 0.5 | 0.4 | 99.2 |

^{*a*} Reaction conditions: HMF (50.4 mg, 0.4 mmol), solvent (8 mL), C–Fe₃O₄–Pd (40 mg, 1.8 mol.%), K₂CO₃ (27.6 mg, 0.2 mmol), oxygen flow rate (30 mL min⁻¹), 80 °C, 4 h. ^{*b*} The reaction temperature was 100 °C. Otherwise, reaction conditions were the same as described above. ^{*c*} The reaction was carried out without K₂CO₃. ^{*d*} Total selectivity of furans is defined as the mole ratio of furan products including FDCA, DFF and HMFCA to the consumed HMF.

neutralized by K₂CO₃, but is absorbed on the catalyst surface, leading to the low catalytic activity. It is interesting to note that different products were produced in DMSO at different reaction temperatures (Table 1, entries 3 vs. 4). DFF yield of 30.0% and HMFCA yield of 10.4% were obtained in DMSO at 80 °C (Table 1, entry 3). However, FDCA was the major product, with a yield of 45.8% in DMSO when the reaction temperature was increased to 100 °C (Table 1, entry 4). Seeing the results in entries 3 & 4, DFF and HMFCA should be the intermediates during the oxidation of HMF into FDCA at 100 °C in DMSO. Among all of the organic solvents tested, C-Fe₃O₄-Pd showed the best catalytic performance in the protic solvent ethanol, with HMF conversion of 61.2% and FDCA yield of 50.4% (Table 1, entry 5). To our pleasure, water proved to the best solvent for the oxidation of HMF into FDCA over the C-Fe₃O₄-Pd catalyst (Table 1, entry 6). High HMF conversion of 87.2% and FDCA yield of 82.3% were achieved in water in the presence of 0.5 equiv of K₂CO₃. The oxidation of HMF using water, a green solvent, and molecular oxygen as the oxidant appears very appealing due to its low cost and nontoxicity. A control experiment was also conducted with the oxidation of HMF in water without K₂CO₃. As expected, the C-Fe₃O₄-Pd catalyst showed poor catalytic performance in water without K₂CO₃ (Table 1, entries 6 vs. 7), confirming the crucial role of the base in obtaining excellent catalytic activity of the C-Fe₃O₄-Pd catalyst for the aerobic oxidation of HMF into FDCA in water. It is also interesting to note that each solvent gave not only different product distributions, but also different total furan selectivity. The lowest total selectivity was observed in toluene, and the highest total selectivity was obtained in water.

Effect of base amount on the aerobic oxidation of HMF into FDCA in water

As discussed above, K_2CO_3 plays a crucial role in the aerobic oxidation of HMF over C-Fe₃O₄-Pd catalyst; therefore, the effect of base amount on this reaction were studied. Compared with the results of using 0.5 equiv of K_2CO_3 (Table 2, entry 1), HMF conversion and FDCA yield increased to 98.7% and 87.6%, respectively, when 1 equiv of K_2CO_3 was used (Table 2, entry 2). It is calculated that FDCA selectivity with 1

 Table 2
 Results of HMF oxidation with different amounts of K₂CO₃^a

| Entry | Mole ratio of K ₂ CO ₃ to HMF | HMF conversion (%) | FDCA yield (%) | FDCA selectivity (%) |
|-------|---|-----------------------|-------------------|-------------------------|
| 1 | 0.5 | 87.2 | 82.3 | 94.4 |
| 2 | 1.0 | 98.7 | 87.6 | 88.8 |
| 3 | 1.5 | 100 | 62.7 | 62.7 |
| 4 | 0.25 | 45.4 | 40.1 | 88.4 |
| 5 | 0.125 | 23.8 | 21.9 | 92.0 |
| 6 | 0 | 12.1 | 11.1 | 91.7 |

 a Reaction conditions: HMF (50.4 mg, 0.4 mmol), H₂O (8 mL), C-Fe₃O₄-Pd (40 mg, 1.8 mol.%), a set amount of K₂CO₃, oxygen flow rate (30 mL min⁻¹), 80 °C, 4 h.

equiv of K₂CO₃ was a little lower than that obtained with 0.5 equiv of K₂CO₃ (Table 2, entries 1 vs. 2). It should be noted that K₂CO₃ also played a negative effect on this reaction, as HMF is not stable under acidic and alkaline conditions. For example, Rass et al. found that the treatment of HMF in Na₂CO₃ (2 equiv) aqueous solution at 100 °C yielded 50% HMF degradation after 2 h.44 This trend was much more apparent with the further increase of K₂CO₃ amount to 1.5 equiv. Full HMF conversion was obtained with FDCA yield of 62.7% by the use of 1.5 equiv of K₂CO₃ (Table 2, entry 3). As 0.5 equiv of K₂CO₃ is the stoichiometric dosage to neutralize the resultant FDCA in theory, the final reaction solution with 1 and 1.5 equiv of K₂CO₃ was alkaline. When the amount of K₂CO₃ was below 0.5 equiv, HMF conversion and FDCA yield gradually decreased with the decrease of K_2CO_3 (Table 2, entries 4-6). For example, HMF conversions were 45.4% and 23.8% using 0.25 and 0.125 equiv of K₂CO₃, respectively, and the corresponding FDCA yields were 40.1% and 21.9%, respectively. The reason was that K₂CO₃ was not sufficient to neutralize the FDCA product, resulting in the loss of catalytic activity during the reaction process.

Effect of reaction temperature on the aerobic oxidation of HMF

The effect of reaction temperature was also studied for the oxidation of HMF over $C-Fe_3O_4$ -Pd catalyst. Experiments were carried out at four different reaction temperatures in

the range of 298 K to 373 K. As shown in Table 3, the aerobic oxidation of HMF is sensitive to the reaction temperature. HMF conversion and FDCA yield increased with an increase of reaction temperature from 298 K to 353 K (Table 3, entries 1, 3 & 4). For example, HMF conversion of 41.3% and FDCA vield of 38.3% were obtained at the reaction temperature of 25 °C (Table 3, entry 1). Increasing the reaction temperature to 60 °C greatly enhanced the reaction efficiency, leading to HMF conversion of 77.6% and FDCA yield of 71.1% (Table 3, entry 3). Further increasing the reaction temperature to 80 °C, HMF conversion and FDCA yield still improved to 87.2% and 82.3%, respectively (Table 3, entry 4). It is interesting to note that the selectivity of FDCA was almost the same, at around 90%, indicating that the side reaction, especially base-promoted degradation of HMF, was not serious in the reaction temperature range from 298 K to 353 K. HMF conversion further increased from 87.2% at 80 °C to 97.1% at 100 °C (Table 3, entries 4 & 5). However, FDCA yield of 80.5% at 100 °C was a little lower than that at 80 °C (Table 3, entries 4 vs. 5). The main reason should be that the base-promoted degradation of HMF became more serious at the higher reaction temperature. For instance, Rass et al. reported that up to 50% HMF was degraded into other byproducts after 2 h at 100 °C in Na₂CO₃ (2 equiv) aqueous solution.⁴⁴ It is worth noting that high HMF conversion of 95.4% and FDCA yield of 87.9% was achieved at room temperature (25 °C) after prolonging the reaction time from 4 h to 12 h (Table 3, entry 2). To the best of our knowledge, there is no report on the oxidation of HMF into FDCA under such mild reaction conditions (e.g. room temperature, atmospheric oxygen pressure, low dosage of base).

Aerobic oxidation of HMF with different catalyst amounts

Experiments were also carried out with different amounts of the catalyst to investigate the effect of catalyst loading. Table 4 shows the results of HMF conversion, FDCA yield and selectivity. Generally, the larger the catalyst dosage was, the higher the HMF conversion and FDCA yield were (Table 4, entries 1–3). HMF conversion of 57.8% and FDCA yield of 52.9% were obtained after 4 h using 20 mg of C–Fe₃O₄–Pd (Table 4, entry 1).

| Table 3 The results of HMF oxidation at different reaction temperatures ^a | | | | | |
|--|------------------|-----------------------|-------------------|-------------------------|--|
| Entry | Temperature (°C) | HMF conversion (%) | FDCA yield (%) | FDCA selectivity (%) | |
| 1 | 25 | 41.3 | 38.3 | 92.7 | |
| 2^{b} | 25 | 95.4 | 87.9 | 92.1 | |
| 3 | 60 | 77.6 | 71.1 | 91.6 | |
| 4 | 80 | 87.2 | 82.3 | 94.4 | |
| 5 | 100 | 97.1 | 80.5 | 82.9 | |

^{*a*} Reaction conditions: HMF (50.4 mg, 0.4 mmol), H_2O (8 mL), C-Fe₃O₄-Pd (40 mg, 1.8 mol%), K_2CO_3 (27.6 mg, 0.2 mmol), oxygen flow rate (30 mL min⁻¹), 4 h. ^{*b*} The reaction time was 12 h under otherwise the same reaction conditions as described above.

It is noted that increasing the catalyst dosage to 40 mg resulted in a sharp increase in HMF conversion (87.2%) and FDCA yield (82.3%) (Table 4, entry 2). The increase in HMF conversion with an increase of catalyst dosage at the same reaction time could be attributed to an increase in the availability and number of catalytically active sites. With further increase of the catalyst amount to 60 mg, HMF conversion continually increased from 87.2% to 98.2%, and the corresponding FDCA yield was 91.8% (Table 4, entry 3). It is worth noting that the selectivity of FDCA was almost the same in each case, suggesting that it had no direct relation with the catalyst amount. As discussed above, the main side reaction was caused by the base-promoted degradation of HMF, which mainly depended on the base concentration and reaction temperature. The high catalytic activity of C-Fe₃O₄-Pd inspired us to carry out the reaction in air, without oxygen flush. To our delight, good results were also observed for the oxidation of HMF in air. HMF conversion of 47.7% and FDCA yield of 43.9% were obtained after 4 h in air, which were lower than those with oxygen flush (Table 4, entries 2 vs. 4). The reason could be that the concentration of oxygen in the reaction solution in air was lower than that with oxygen flush. After prolonging the reaction time to 12 h, oxidation of HMF in air also afforded an excellent FDCA yield of 85.7% (Table 4, entry 5). The excellent results of the aerobic oxidation of HMF in air make this method easily handled and economic in practical application. Control experiments were also carried out using graphene oxide-Fe₃O₄ as the catalyst, which was prepared by the same method as the C-Fe₃O₄-Pd catalyst without the addition of Na₂PdCl₄ during the preparative procedure. No FDCA was determined in the oxidation of HMF over graphene oxide-Fe₃O₄ catalyst (Table 4, entry 6), which indicated that Pd nanoparticles were the active sites for the oxidation of HMF into FDCA. The conversion of HMF in entry 6 was caused by the base-promoted degradation of HMF into other byproducts.

Catalyst recycling experiments and large-scale reaction

Facile recycling and high stability are important characteristics of magnetic catalysts. Therefore, experiments on catalyst recycling were also studied. As shown in Fig. 6, after reaction, the C-Fe₃O₄-Pd catalyst was easily collected from the reaction mixture by a permanent magnet. Then, the liquid solution was decanted, and the spent catalyst was washed with water three times and ethanol twice. Finally, the spent catalyst was dried under vacuum at 50 °C overnight. The spent catalyst was used for a second run under the same reaction conditions as described for the first run. As shown in Fig. 7, FDCA yields were almost the same, at about 91%. The results indicate that the C-Fe₃O₄-Pd catalyst was stable during the reaction process without the loss of its catalytic activity. In addition, the stability of the catalyst was also confirmed by ICP-AES. No palladium was determined in the reaction solution, which indicated that there was no leach of palladium from the catalyst to the reaction solution. The stability of the

Table 4 The results of HMF oxidation with different catalyst loading⁴

Catalysis Science & Technology

| Entry | Time (h) | Catalyst amount | HMF conversion (%) | FDCA yield (%) | FDCA selectivity (%) |
|-----------------------|----------|------------------|--------------------|----------------|----------------------|
| 1 | 4 | 20 mg, 0.9 mmol% | 57.8 | 52.9 | 91.5 |
| 2 | 4 | 40 mg, 1.8 mol% | 87.2 | 82.3 | 94.4 |
| 3 | 4 | 60 mg, 2.7 mol% | 98.2 | 91.8 | 93.5 |
| 4^b | 4 | 40 mg, 1.8 mol% | 47.7 | 43.9 | 92.0 |
| 5^b | 12 | 40 mg, 1.8 mol% | 94.4 | 85.7 | 90.8 |
| 6 ^{<i>c</i>} | 4 | 60 mg, 2.7 mol% | 13.0 | 0 | 0 |

^{*a*} Reaction conditions: HMF (50.4 mg, 0.4 mmol), a certain amount of the C–Fe₃O₄–Pd catalyst, water (8 mL), K₂CO₃ (27.6 mg, 0.2 mmol), oxygen flow rate (30 mL min⁻¹), 80 °C, 4 h. ^{*b*} The reaction was carried out in air. Otherwise, reaction conditions were the same as above. ^{*c*} Graphene oxide–Fe₃O₄ was used as the catalyst for the same reaction.



Fig. 7 Recycling experiments of the C–Fe₃O₄–Pd catalyst. Reaction conditions: HMF (50.4 mg, 0.4 mmol), H₂O (8 mL), K₂CO₃ (27.6 mg, 0.2 mmol), oxygen flow rate (30 mL min⁻¹), C–Fe₃O₄–Pd (60 mg, 2.7 mol%), 80 °C, 4 h.

prepared C–Fe₃O₄–Pd catalyst was the same as that reported by Villa *et al.*⁴⁵ They used active carbon-supported, bimetallic nanoparticles (Au₈Pd₂/AC) for the oxidation of HMF into FDCA and found that it was stable during the recycling experiment.

Finally, the large-scale oxidation of HMF into FDCA was also carried out. 1 g of HMF was used as the starting material. As the reaction required neutralization of the formed FDCA, 0.5 equiv of Na₂CO₃ (0.55 g) was used. 1 g of HMF and 0.55 g of Na₂CO₃ were added into 100 mL of water, and then the reaction was carried out at 80 °C by the use of 0.5 g of C-Fe₃O₄-Pd with oxygen flow rate at 30 mL min⁻¹. Thinlayer chromatography was used to track the reaction process. After 12 h reaction, HMF completely disappeared. Then, the catalyst was removed, and the reaction solution was concentrated by reducing evaporation. Then, the resulting residues were purified on silica gel, eluting with methanol/ethyl acetate. The amount of isolated FDCA was 1.05 g, equaling a yield of 84.8%. Compared with the above microreaction, the large-scale reaction yield was a little lower.

Conclusion

In this study, the superparamagnetic C–Fe $_3O_4$ –Pd catalyst was successfully prepared by a one-pot solvothermal route,

and it showed high catalytic activity in the aerobic oxidation of HMF into FDCA in water under mild reaction conditions. Results demonstrated that reaction temperature and base concentration greatly affected not only the oxidation of HMF, but also its degradation. Under optimal reaction conditions, high HMF conversion of 98.2% and FDCA yield of 91.8% were obtained after 4 h at 80 °C with a K₂CO₃/HMF molar ratio of 0.5. Excellent results were also achieved by the oxidation of HMF over C-Fe₃O₄-Pd catalyst in air and at room temperature with an appropriate reaction time. More importantly, the catalyst was easily recovered by an external magnet and reused without the loss of its catalytic activity. Compared with other reported methods, the present catalytic system showed three distinct advantages: the use of stoichiometric amount of base, high activity under atmospheric oxygen pressure, and facile catalyst recycling. It is believed that this finding provides an efficient, green and sustainable method for the production of other valuable chemicals by the oxidation of various biomass-derived hydroxyl compounds.

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Paper

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