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Efficient oxidation of biomass derived 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid catalyzed by Merrifield resin supported cobalt porphyrin

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HIGHLIGHTS

- Selective oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid was developed.
- Co(II)–meso-tetra(4-pyridyl)-porphyrin showed high catalytic activity for this reaction.
- HMF conversion of 95.6% and FDCA yield of 90.4% were obtained.

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ABSTRACT

In this study, a new method was developed for the oxidation of 5-hydroxymethylfurfural (HMF) into 2,5-furandicarboxylic acid (FDCA) over Merrifield resin supported Co(II)–meso-tetra(4-pyridyl)-porphyrin (abbreviated as Merrifield resin-Co-Py). Diffuse reflectance spectra showed that Co(II)–meso-tetra(4-pyridyl)-porphyrin was successfully bonded on the Merrifield resin. The Merrifield resin-Co-Py catalyst was used for the oxidation of HMF into FDCA, and several parameters were studied. Tert-butyl hydroperoxide was the best oxidant among other common oxidants. The reaction solvent greatly affected both HMF conversion and product selectivity. High HMF conversion of 95.6% and FDCA yield of 90.4% were obtained at 100 °C after 24 h. Time course of HMF conversion over Merrifield resin-Co-Py showed that 2,5-diformylfuran was the intermediate for the conversion of HMF into FDCA. The catalyst could be reused without the significant loss of its catalytic activity.

1. Introduction

With the diminish of fossil resource, much effort has been devoted to the search of the renewable resources for the production of chemicals and fuels for our society [1,2]. Biomass, which is one of the most abundant renewable resources, has been regarded as an important alternative to fossil resource [3,4]. In addition, biomass is the only carbon-containing renewable resource. Therefore, it is the only renewable resource to provide both chemicals and liquid fuels. Biomass conversion is of great importance in terms of green and sustainable chemistry. It is estimated that nearly 18% of all the manufactured chemicals will originate from biomass by the year of 2020. Therefore, a great deal of effort has been devoted to the conversion of biomass into chemicals and fuels [5–7].

5-Hydroxymethylfurfural (HMF) contains one hydroxyl group and a formyl group together with a furan ring, which can be generated from the dehydration of carbohydrates. HMF has been regarded as one of the most versatile and important building blocks for the production of valuable chemicals and fuels through specific catalytic transformation [8]. Consequently, there is a great interest in the synthesis of HMF from various carbohydrates. There were many fruitful results for the synthesis of HMF from monosaccharide, polysaccharides even cellulose and lignocellulose in various catalytic systems [9–13]. However, the production of HMF derivatives is partly impeded due to limited availability of technology for converting HMF into important chemicals.

Catalytic oxidation reaction is one important type of chemical reactions. Through the selective oxidation of HMF, several value added furan compounds can be obtained, such as 2,5-diformylfuran (DFF) [14], 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) [15], and 2,5-furandicarboxylic acid (FDCA) [16]. The structure of FDCA contains two carboxylic acid groups, which is similar with

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the structure of terephthalic acid. Thus, FDCA can be used a potential replacement for the terephthalic acid monomer in the production of polyethyleneterephthalate (PET plastic). In recent years, a great attention has been paid to the catalytic oxidation of HMF into FDCA. Recently, homogeneous catalysts [$Co(OAc)_2/Zn(OAc)_2/NaBr$] were reported for the aerobic oxidation of HMF into FDCA with a yield of 60% [17]. However, it is not economical and environment-friendly to use homogeneous catalysts, as they are difficult to recycle. Unlike homogeneous catalysts, heterogeneous catalysts can be easily separated from the reaction mixture and reused. Therefore, much effort was devoted to the synthesis of FDCA from HMF using various heterogeneous catalysts. Generally, inorganic materials supported noble metals such as Pd, Pt, and Au showed high catalytic activity for the oxidation of HMF [18–22]. Particularly, Au nanoparticles supported on inorganic supports showed excellent catalytic activity and high selectivity. For example, Casanova et al. reported that HMF was selectively converted into FDCA with a yield up to 99% in highly basic conditions under 10 bar air pressure over Au/CeO_2 catalyst [23]. However, these methods still showed some drawbacks such as the high cost of noble metal catalyst, the use of excessive NaOH and high oxygen pressure. There were also some reports on the oxidation of HMF into FDCA by the use of t-BuOOH as the oxidant. For example, full HMF conversion was achieved in the presence of $CuCl_2$, but FDCA yield was only 45% [24]. Recently, magnetic Fe_3O_4–CoO_x showed high catalytic activity for the oxidation of HMF into FDCA. High HMF conversion of 97.2% and FDCA yield of 68.6% were obtained [25]. Therefore, it is still of great importance to explore new catalytic systems for the mild oxidation of HMF into FDCA.

Metalloporphyrin is an important large class of macrocycle compounds. It can be used as a biomimetic catalyst model for the cytochrome P450 enzyme in the hydroxylation of hydrocarbons. In 1979, Groves reported for the first time the use of a metalloporphyrin-based catalytic system for alkene epoxidation [26]. Since then metalloporphyrins-based catalytic systems have been successfully used as biomimetic models of cytochrome P450 spread all over the world. Many improvements have been disclosed in the literature, such as the appearance of more oxidative resistant catalysts or the development of hetero-generous catalysts, namely through the immobilization on several organic/inorganic supports using a wide range of approaches [27]. For example, Du et. al. [28] prepared Merrifield resin supported manganese(III) porphyrin and found that the catalyst showed high stability in the epoxidation of cholest-5-ene derivatives. However, there were few reports on the use of metalloporphyrin in biomass conversion. Herein, with the aim of the development of sustainable chemistry in mind, the commercially available Merrifield resin was used to immobilize cobalt(II)–meso-tetra(4-pyridyl)-porphyrin to construct a heterogeneous catalyst, and used for the oxidation of HMF into FDCA.

2. Experimental

2.1. Materials and methods

Merrifield resin was purchased from Aladdin Chemicals Co., Ltd. (Beijing, China). 4-Pyridinealdehyde and propionic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). HMF (98%) was supplied by Beijing Chemicals Co., Ltd. (Beijing, China). FDCA and DFF were purchased from the J&K Chemical Co., Ltd., (Beijing, China). Acetonitrile (HPLC grade) was purchased from Tedia Co. (Fairfield, USA). Other chemicals and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Synthesis of 5,10,15,20-tetra(4-pyridyl)-porphyrin

Pyrrole (2.5 g) in 40 mL of propionic acid was added dropwise into a mixed solution of 4-pyridinecarboxaldehyde (4.3 g) in 150 mL of propionic acid at 150 °C with a magnetic stirring. After the complete addition, the reaction mixture was heated at reflux temperature for 2 h. Then 50 mL of ethyl alcohol was added, and the mixture was placed in the refrigerator for 24 h. Black precipitates were observed at the bottom of the flask, and then filtered, washed with petroleum ether, dried in an vacuum oven at 40 °C overnight. Finally, violet black crystal was obtained in a yield of 12.3%. ^1H NMR ($CDCl_3$): δ 2.9 ppm (2H, N–H), δ 9.0 ppm (8H, pyridine), δ 8.9 ppm (4H, pyridine), δ 8.1 ppm (8H, pyrrole); UV–Vis, $\lambda_{max/nm}$: 443 nm, 546 nm, 586 nm, 642 nm.

2.3. Synthesis of cobalt(II)–meso-tetra(4-pyridyl)-porphyrin

Cobalt(II)–meso-tetra(4-pyridyl)-porphyrin was prepared by the reaction of 5,10,15,20-Tetra(4-pyridyl)-porphyrin (1.0 g) and cobalt(II) acetate (0.4 g) in DMF (10 mL) at the reflux temperature for 4 h. Then the reaction mixture was cooled down to room temperature and dumped into H_2O (50 mL) for 2 h. The precipitate was filtered and washed with H_2O. Finally, the crude product was purified on a silica gel (petroleum ether/dichloromethane: 1/1). Cobalt(II)–meso-tetra(4-pyridyl)-porphyrin (1.19 g) was obtained in a yield of 85%. UV–Vis: $\lambda_{max/nm}$: 445 nm, 542 nm, 647 nm.

2.4. Preparation of the Merrifield resin supported cobalt(II)–meso-tetra(4-pyridyl)-porphyrin

Due to the solubility of cobalt(II)–meso-tetra(4-pyridyl)-porphyrin was dissolved in the reaction solvents, it is difficult to recycle the catalyst. Therefore, it needed a support to fix cobalt(II)–meso-tetra(4-pyridyl)-porphyrin. Merrifield resin was used to support cobalt(II)–meso-tetra(4-pyridyl)-porphyrin by the solid–liquid phase reaction. Cobalt(II)–meso-tetra(4-pyridyl)-porphyrin (10.3 mg) and Merrifield resin (0.41 g) were added into DMF (25 mL), and the mixture was heated at 160 °C with a magnetic stirring for 18 h. Then the solid catalyst was filtered, and washed with DMF (25 mL) to remove the physical absorbed cobalt(II)–meso-tetra(4-pyridyl)-porphyrin. The loading of cobalt(II)–meso-tetra(4-pyridyl)-porphyrin on Merrifield resin was calculated by the change of UV–Vis absorbance of cobalt(II)–meso-tetra(4-pyridyl)-porphyrin in the mixed solution before and after adsorption of the resin, and the content of cobalt(II)–meso-tetra(4-pyridyl)-porphyrin was equal to 1.4 wt.%. The as-prepared catalyst was abbreviated as Merrifield resin-Co-Py in the following.

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

Experiments for the aerobic oxidation of HMF were carried out in a 10 mL round bottom flask. Typically, HMF (70 mg) was added into acetonitrile (5 mL), and the mixture was stirred vigorously to give a clear solution. Then Merrifield resin-Co-Py catalyst (50 mg) and 70% aqueous tert-butyl hydroperoxide solution (TBHP) (0.5 mL, 5 mmol) were added into the reaction solution. The reaction was carried out at 110 °C for the desired reaction time, and time zero was recorded after the addition of TBHP.

2.6. Analytic methods

The amounts of HMF and FDCA in the reaction mixture were performed on a VARIAN ProStar 210 HPLC system. Samples were separated by a reversed-phase C18 column (200 × 4.6 mm) with a detection wavelength of 280 nm. The mobile phase was constituted of acetonitrile and 0.1 wt.% acetic acid aqueous solution (V:V = 30: 70) at 1.0 mL min^{-1}. The column oven temperature was kept at 25 °C. The content of HMF and DFF in samples were calculated by the external standard calibration curve method, which were constructed based on the pure compounds.

HMF conversion = moles of converted HMF/moles of starting HMF × 100%

FDCA yield = moles of FDCA/moles of starting HMF × 100%

3. Results and discussion

3.1. Catalyst preparation and characterization

The procedure of the preparation of Merrifield resin-Co-Py catalyst is illustrated in Scheme 1. Firstly, metal free 5,10,15,20-tetra(4-pyridyl)-porphyrin was prepared by the reaction of pyrrole and 4-pyridinealdehyde in the presence of propanoic acid. Coordination of Co^{2+} into metal-free porphyrin was carried out by the reaction of $Co(OAc)_2$ with metal-free porphyrin (1) at reflux temperature, giving rise to cobalt(II)–meso-tetra(4-pyridyl)-porphyrin (2) in a yield of 85%. The solid support used to immobilize the cobalt(II)–meso-tetra(4-pyridyl)-porphyrin (2) is the well known Merrifield resin, a chloromethylated styrene–divinylbenzene copolymer, in which the benzyl chloride in the Merrifield resin reacts with the peripheral pyridine groups of (2) to immobilize (2). The quaternization reaction was carried out by the treatment of (2) with Merrifield resin. After the immobilization of (2) on Merrifield resin, the crude catalyst was washed with DMF several times to remove any physically absorbed (2) until the filter showed no UV–Vis absorption. Fig. 1 shows the diffuse reflectance spectra of Merrifield resin-Co-Py (3) and the support Merrifield resin. It is only observed a strong absorption peak at 270 nm in Merrifield resin, which was assigned to the absorption of aromatic ring in Merrifield resin. Besides the absorption band at 270 nm, an absorption band around 649 nm was observed with the Merrifield resin-Co-Py catalyst (Fig. 2, curve b), which was called Q-band due to $\pi \rightarrow \pi^*$ transition of porphyrin core [29]. In addition, a peak at 442 nm was also observed with the Merrifield resin-Co-Py catalyst, which was called by B-band due to $\pi \rightarrow \pi*$ transition of porphyrin core [24]. These results clearly indicated that Co-Py was successfully immobilized on Merrifield resin by covalent connection.

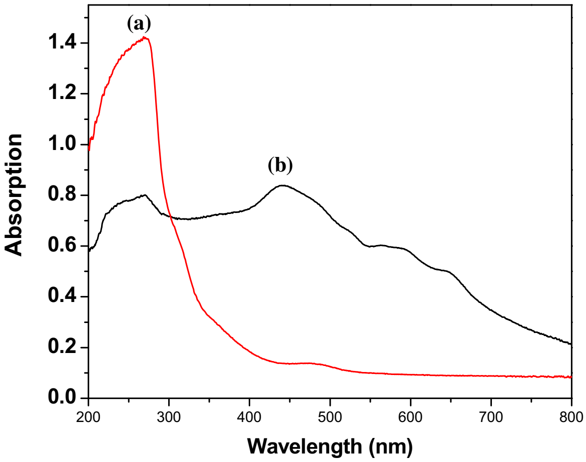


Fig. 1. Diffuse reflectance spectra of the samples. (a) Merrifield resin; (b) Merrifield resin-Co-Py.

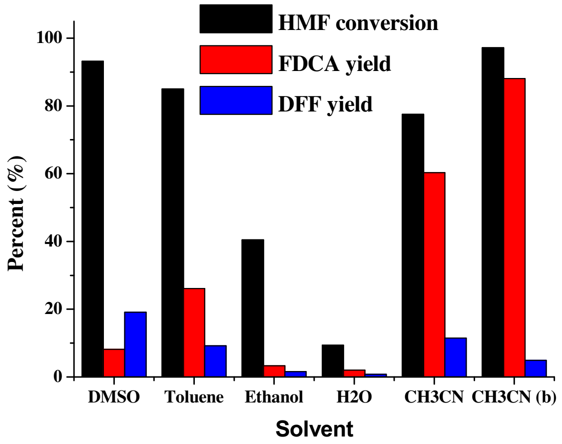
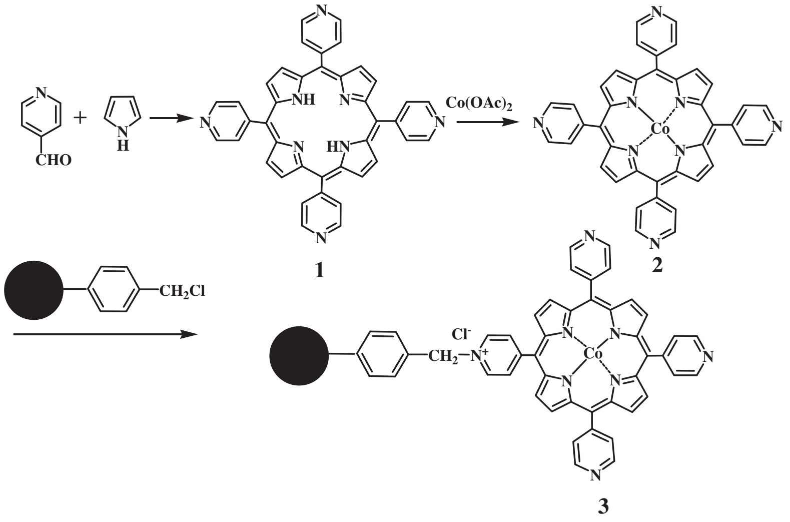


Fig. 2. Effect of the solvents on the aerobic oxidation of HMF into DFF. Reaction conditions: Merrifield resin-Co-Py (50 mg), HMF (70 mg), 70 °C, t-BuOOH (5 mmol), CH_3CN (5 mL), 24 h; [b] the reaction time was 48 h.



Scheme 1. Schematic illustration of the preparation of Merrifield resin-Co-Py.

3.2. Catalytic oxidation of HMF into FDCA using various oxidants

The catalytic activity of the Merrifield resin-Co-Py catalyst was evaluated by the oxidation of HMF. Firstly, several common oxidants were used for the oxidation of HMF over Merrifield resin-Co-Py catalyst. As shown in Table 1, the oxidant showed a remarkable effect on the oxidation of HMF. HMF conversion was low in the presence of molecular oxygen (Table 1, Entry 1). It was reported that isobutyraldehyde could improve the efficiency of the oxidation of alcohols [30]. As shown in Table 1, HMF conversion and products yields indeed largely increased (Table 1, Entry 2), but HMF conversion was still low in 65.6% after 12 h. The reason is that metalloporphyrins could react with isobutyraldehyde to generate high-valent metal-oxo intermediate in the presence of molecular oxygen, which was considered to be the reactive intermediate in the oxidation reaction [30]. The highest HMF conversion of 96.5% was obtained when sodium periodate ($NaIO_4$) was used, but both DFF yield and FDCA yield were very low (Table 1, Entry 3). The reason should be that furan ring in HMF was destroyed due to the strong oxidative ability of $NaIO_4$. Low HMF conversion was observed when the mild oxidant H_2O_2 was used (Table 1, Entry 4). HMF conversion of 77.5% and FDCA yield of 60.3% were obtained after 24 h while using TBHP as the oxidant (Table 1, Entry 5). In addition, DFF was also obtained in a yield of 11.5% (Table 1, Entry 5). Control experiment was also carried out without catalyst. It was found that HMF conversion was very low, which indicated that Merrifield resin-Co-Py catalyst promoted the oxidation of HMF. Besides O_2 and H_2O_2, the use of TBHP as an oxidant has also been popular in modern organic syntheses as it is moderately active toward most organic substrates, easily available and can be used for large scale synthesis.

3.3. Catalytic oxidation of HMF into FDCA in various solvents

The effect of the oxidation of HMF was carried out in various solvent and the results are summarized in Fig. 2. Seeing from Fig. 2, it was observed that the solvent showed a remarkable effect both on HMF conversion and product selectivity. High HMF conversion was obtained in dimethyl sulfoxide (DMSO) and toluene, but the total yield of FDCA and DFF was low. Moderate HMF conversion and low products yields were obtained in low boiling point aprotic ethanol. The lowest HMF conversion was obtained when the oxidation reaction was carried out in H_2O. Under otherwise the same reaction conditions, the best catalytic performance of Merrifield resin-Co-Py was obtained when the reaction was carried out in CH_3CN. HMF conversion of 77.5% and FDCA yield of 60.3% were obtained after 24 h. Further increasing the reaction time to 48 h, high HMF conversion of 97.2% and FDCA yield of 88.1% were obtained in CH_3CN. The properties of the solvents such as the polarity, dielectric constant, steric hindrance, acid-base property should show some effect on the oxidation of HMF by the use of t-BuOOH over the Merrifield resin-Co-Py catalyst [31].

Table 1
Catalytic oxidation of HMF into FDCA using various oxidants.[a]

Entry	Oxidant	Time (h)	HMF conversion (%)	FDCA yield (%)	DFF yield (%)
1	O_2	24	8.7	0	1.3
2[b]	O_2	12	65.6	16.7	43.2
3	$NaIO_4$	24	96.5	3.9	3.5
4	H_2O_2	24	14.8	4.2	2.8
5	t-BuOOH	24	77.5	60.3	11.5
6[c]	t-BuOOH	24	3.6	0.3	1.2

[a] Reaction conditions: HMF (70 mg), Merrifield resin-Co-Py (50 mg), 70 °C, CH_3CN (5 mL), 24 h, 5 mmol of oxidant; In the case of O_2, O_2 was flowed at a rate of 30 ml min^{-1}.
[b] Isobutyraldehyde was used.
[c] The reaction was carried out in the absence of the catalyst.

3.4. Catalytic oxidation of HMF into FDCA at different reaction temperatures

The effect of reaction temperature on the oxidation of HMF was also investigated, and the results are shown in Table 2. It was observed that both HMF conversion and FDCA selectivity were greatly affected by the reaction temperature. HMF conversion increased with the increase of reaction temperature from 40 °C to 100 °C. A low HMF conversion of 17.2% was only obtained after 24 h at a low reaction temperature of 40 °C, while it sharply reached 77.5% at 70 °C after 24 h (Table 2, Entries 1 & 2). HMF conversion further increased to 95.6% after 24 h when the reaction temperature further increased to 100 °C (Table 2, Entry 3). It was also found that FDCA yield and selectivity increased with the increase of reaction temperature. The highest FDCA yield of 90.4% and the selectivity of 94.5% were obtained at 100 °C after 24 h (Table 2, Entry 3). In addition, DFF was also determined as one of the oxidation products, which is the intermediate for the conversion of HMF into FDCA. It was calculated that the ratio of FDCA to DFF increased with the increase of reaction temperature, which indicated that the increase of the reaction temperature promoted the oxidation of HMF into DFF, and the further oxidation of DFF into FDCA. Higher HMF conversion and FDCA yield at higher reaction temperature indicated that much more active molecules were formed, leading to a higher reaction rate.

3.5. Time course of the oxidation of the oxidation of HMF

In order to give more insights into the oxidation of HMF into FDCA over the Merrifield resin-Co-Py catalyst, the amounts of the products at different reaction time points were recorded, and the results are shown Table 3. HMF conversion gradually increased during the reaction process. HMF conversion was only 17.4% after 2 h, while that was 97.2% after 48 h. The yield of FDCA also gradually increased with an increase of the reaction time, and the maximum FDCA yield was obtained in 88.1% after 48 h. Besides of FDCA, DFF was also formed during the oxidation process. The yield of DFF firstly increased, and then it decreased gradually. The maximum DFF yield was obtained in 20.6% after 8 h. In addition to DFF, HMFCA was also detected, but the yield of HMFCA was in a low level around 1.5%. These results confirmed that DFF and HMFCA were both the intermediates during the oxidation of HMF into FDCA. These results indicated that the hydroxyl group in HMF was preferable to be oxidized rather than the aldehyde group in HMF. Therefore, the oxidation of HMF into DFF, and the further oxidation of DFF into FDCA was the main reaction routs for the oxidation of HMF into FDCA over Merrifield resin-Co-Py catalyst (Scheme 2). The reaction process was almost the same with the oxidation of HMF into FDCA using $Fe_3O_4–CoO_x$ catalyst [25].

Table 2
The effect of reaction temperature on the oxidation of HMF.[a]

Entry	Reaction temperature (°C)	HMF conversion (%)	DFF yield (%)	FDCA yield (%)	FDCA selectivity (%)
1	40	17.2	9.6	6.6	38.4
2	70	77.5	14.5	60.3	77.8
3	100	95.6	2.4	90.4	94.5

[a] Reaction conditions: Merrifield resin-Co-Py (50 mg), HMF (70 mg), t-BuOOH (5 mmol), CH_3CN (5 mL), 24 h.

Table 3
Time course of products distribution during the oxidation of HMF.[a]

Entry	Time (h)	HMF conversion (%)	FDCA yield (%)	DFF yield (%)	HMFCA yield (%)
1	2	17.4	6.3	8.7	1.4
2	4	27.8	10.1	13.2	1.7
3	8	40.1	15.5	20.6	1.2
4	12	54.1	32.3	16.8	1.7
5	24	77.5	60.3	11.5	1.5
6[c]	36	94.7	82.8	5.8	1.5
7	48	97.2	88.1	2.9	1.0

[a] Merrifield resin-Co-Py (50 mg), HMF (70 mg), t-BuOOH (5 mmol), CH_3CN (5 mL), 24 h.

3.6. Comparison our method for the synthesis of FDCA from HMF with other reported methods

In order to evaluate the advantages of our catalytic system for the synthesis of FDCA from the oxidation of HMF, the developed method in this study was compared with the recent reported methods for the synthesis of FDCA, and the results are shown in Table 4. The use of oxygen was preferred to the use of t-BuOOH. However, it generally required to the use of high pressure oxygen, which was not safe for chemical reactions. As shown in Table 4, Entry 1, although the use $Co(OAc)_2/Zn(OAc)_2/Br^-$ under 10 bar oxygen pressure gave full HMF conversion, the yield of FDCA was low in 60%. In addition, the homogeneous catalyst could not be recycled. Currently, supported noble metals were reported to be the most popular methods. High HMF conversion and FDCA yield were always obtained (Table 4, Entries 2 and 3). These methods required to use high oxygen pressure and high concentration of alkaline. More importantly, these methods were not economic due to the high cost of noble metals. There were also some reported on the use of t-BuOOH as the oxidant. Poor FDCA yield and selectivity were obtained using the homogeneous $CuCl_2$ (Table 4, Entry 4), and high HMF conversion and moderate FDCA yield were achieved in the presence of Fe_3O_4–CoO_x catalyst. Compared with all of the typical methods as discussed above, our method did not required to carry out under high oxygen pressure and high concentration of alkaline. Furthermore, the cost of catalyst was much lower than the noble metal catalyst. In addition, as shown in the following part, the catalyst was stable and could be reused for several times.

3.7. Catalyst recycling experiments and product purification

Recycle of heterogeneous catalysts is one of the important goals in terms of green chemistry. Therefore, the oxidation of HMF in CH_3CN was used as a model reaction to study the stability of the Merrifield resin-Co-Py catalyst. Reactions were carried out at 70 °C for 24 h. After reaction, the catalyst was collected by centrifugation in order to avoid the loss of catalyst. Then the spent catalyst was washed three times with ethanol, and dried at 60 °C over night in a vacuum oven. The spent catalyst was reused for the next cycle under the same reaction conditions. The results of recycling of Merrifield resin-Co-Py catalyst is Fig. 3. As shown in Fig. 3, the yield of FDCA kept stable around 60%, and there was no significant decrease of FDCA yield. There results clearly indicated that the Merrifield resin-Co-Py catalyst was stable and its catalytic activity was remained during the reaction process. Our results were the same with the results reported by the Du et. al. [28], in which, Merrifield resin supported manganese(III) porphyrins showed high stability in the epoxidation of cholest-5-ene derivatives.

Table 4
Comparison our method for the oxidation of HMF into FDCA with other methods.

Entry	Catalyst	T (°C)	Oxidant	HMF Con. (%)	FDCA yield (%)	Refs.
1	$Co(OAc)_2/Zn(OAc)_2/Br^-$	90	10 bar O_2	100	60	[17]
2	Au/CeO_2	65	10 bar O_2	100	99	[23]
3	Fe_2O_3@HAP-Pd(0)	100	Atmospheric pressure O_2	97	92.9	[22]
4	$CuCl_2$	25	t-BuOOH	100	45	[24]
5	Fe_3O_4–CoO_x	80	t-BuOOH	97.2	68.6	[25]
6	Merrifield resin-Co-Py	100	t-BuOOH	95.6	90.4	This work

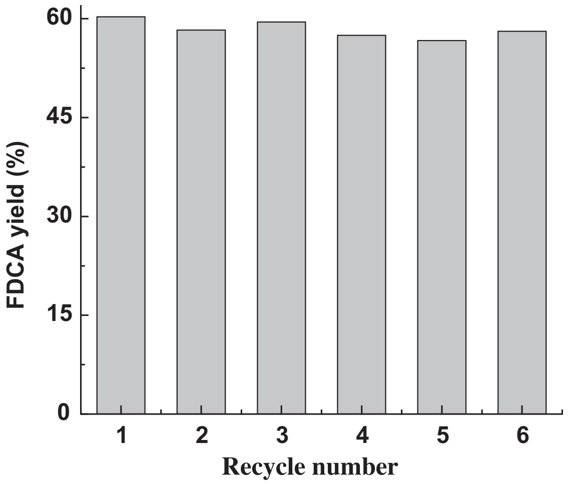
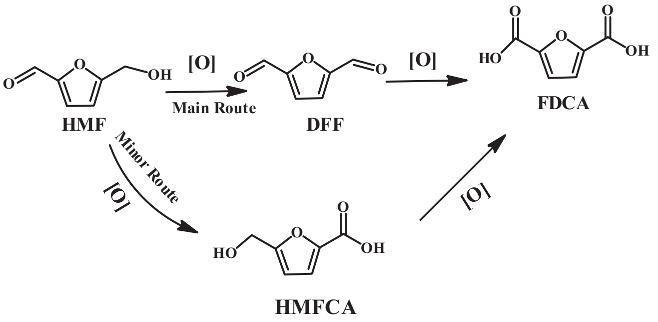


Fig. 3. Recycle experiments of the catalyst. Reaction conditions: Merrifield resin-Co-Py (50 mg), HMF (70 mg), t-BuOOH (5 mmol), CH_3CN (5 mL), 24 h.



Scheme 2. The proposed catalytic routes for the oxidation of HMF into FDCA over Merrifield resin-Co-Py catalyst.

4. Conclusions

In summary, a new method was developed for the oxidation of HMF into FDCA by the use of Merrifield resin-Co-Py as the catalyst. Some important reaction parameters were studied to optimize the oxidation of HMF. Several parameters were studied, and it was found that the oxidant and the solvent showed great affect on the oxidation of HMF into FDCA. t-BuOOH was found to be the best oxidant among other common oxidants, and CH_3CN was proved to be the best solvent. High HMF conversion of 95.6% and FDCA yield of 90.4% were obtained at 100 °C after 24 h. DFF was the main intermediate in the conversion of HMF into FDCA. More importantly, the catalyst could be reused without the significant loss of its catalytic activity.

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References

[1] P. Gallezot, Conversion of biomass to selected chemical products, Chem. Soc. Rev. 41 (2012) 1538–1558.

[2] D. Mansur, T. Tago, T. Masuda, H. Abimanyu, Conversion of cacao pod husks by pyrolysis and catalytic reaction to produce useful chemicals, Biomass Bioenergy 66 (2014) 275–285.

[3] B. Chamnankid, C. Ratanatawanate, K. Faungnawakij, Conversion of xylose to levulinic acid over modified acid functions of alkaline-treated zeolite Y in hot-compressed water, Chem. Eng. J. 258 (2014) 341–347.

[4] J.J. Bozell, Connecting biomass and petroleum processing with a chemical bridge, Science 329 (2010) 522–523.

[5] D. Kim, K. Lee, K.Y. Park, Hydrothermal carbonization of anaerobically digested sludge for solid fuel production and energy recovery, Fuel 130 (2014) 120–125.

[6] M. Besson, P. Gallezot, C. Pinel, Conversion of biomass into chemicals over metal catalysts, Chem. Rev. 114 (2014) 1827–1870.

[7] Y. Xiong, Z.H. Zhang, X. Wang, B. Liu, J.T. Lin, Hydrolysis of cellulose in ionic liquids catalyzed by a magnetically-recoverable solid acid catalyst, Chem. Eng. J. 235 (2014) 349–355.

[8] R.J. van Putten, J.C. van der Waal, E. de Jong, C.B. Rasrendra, H.J. Heeres, J.G. de Vries, Hydroxymethylfurfural, A versatile platform chemical made from renewable resources, Chem. Rev. 113 (2013) 1499–1597.

[9] S. Xiao, B. Liu, Y. Wang, Z. Fang, Z. Zhang, Efficient conversion of cellulose into biofuel precursor 5-hydroxymethylfurfural in dimethyl sulfoxide-ionic liquid mixtures, Bioresour. Technol. 151 (2014) 361–366.

[10] Z. Zhang, B. Liu, Z.K. Zhao, Conversion of fructose into 5-HMF catalyzed by $GeCl_4$ in DMSO and [Bmim]Cl system at room temperature, Carbohydr. Polym. 88 (2012) 891–895.

[11] T.F. Wang, M.W. Nolte, B.H. Shanks, Catalytic dehydration of C_6 carbohydrates for the production of hydroxymethylfurfural (HMF) as a versatile platform chemical, Green Chem. 16 (2014) 548–572.

[12] Z.F. Fang, B. Liu, J.J. Luo, Y.S. Ren, Z.H. Zhang, Efficient conversion of carbohydrates into 5-hydroxymethylfurfural catalyzed by the chromium-exchanged montmorillonite K-10 clay, Biomass Bioenergy 60 (2014) 171–177.

[13] J.B. Binder, R.T. Raines, Simple chemical transformation of lignocellulosic biomass into furans for fuels and chemicals, J. Am. Chem. Soc. 131 (2009) 1979–1985.

[14] B. Liu, Z.H. Zhang, J.J. Luo, Z.F. Fang, H.M. Duan, Efficient aerobic oxidation of biomass-derived 5-hydromethylfurfural to 2,5-diformylfuran catalyzed by magnetic nanoparticle supported manganese oxide, Appl. Catal., A 472 (2014) 64–71.

[15] Z. Zhang, B. Liu, K. Lv, J. Sun, K. Deng, Aerobic oxidation of biomass derived 5-hydroxymethylfurfural into 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) catalyzed by montmorillonite K-10 clay immobilized molybdenum acetylacetonate complex, Green Chem. 16 (2014) 2762–2770.

[16] O. Casanova, S. Iborra, A. Corma, Biomass into chemicals: aerobic oxidation of 5-hydroxymethyl-2-furfural into 2,5-furandicarboxylic acid with gold nanoparticle catalysts, ChemSusChem 2 (2009) 1138–1144.

[17] B. Saha, S. Dutta, M.M. Abu-Omar, Aerobic oxidation of 5-hydroxylmethylfurfural with homogeneous and nanoparticulate catalysts, Catal. Sci. Technol. 2 (2012) 79–81.

[18] E. Davis, L.R. Houk, E.C. Tamargo, A.K. Datye, R.J. Davis, Oxidation of 5-hydroxymethylfurfural over supported Pt, Pd and Au catalysts, Catal. Today 160 (2011) 55–60.

[19] X.Y. Wan, C.M. Zhou, J.S. Chen, W.P. Deng, Q.H. Zhang, Y.H. Yang, Y. Wang, Base-free aerobic oxidation of 5-hydroxymethyl-furfural to 2,5-furandicarboxylic acid in water catalyzed by functionalized carbon nanotube-supported Au–Pd alloy nanoparticles, ACS Catal. 4 (2014) 2175–2185.

[20] B. Liu, Y.S. Ren, Z.H. Zhang, Aerobic oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid in water under mild conditions, Green Chem. (2015), http://dx.doi.org/10.1039/c4gc02019g.

[21] N.K. Gupta, S. Nishimura, A. Takagaki, K. Ebitani, Hydrotalcite-supported gold-nanoparticle-catalyzed highly efficient base-free aqueous oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxlc acid under atmospheric oxygen pressure, Green Chem. 13 (2011) 824–827.

[22] Z.H. Zhang, J.D. Zhen, B. Liu, K.L. Lv, K.J. Deng, Selective aerobic oxidation of biomass derived precursor 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid under mild conditions over a magnetic palladium nanocatalyst, Green Chem. 17 (2015) 1308–1317.

[23] Y.Y. Gorbanev, K.S. Klitgaard, J.M. Woodley, C.H. Christensen, A. Riisager, Gold-catalyzed aerobic oxidation of 5-hydroxymethylfurfural in water at ambient temperature, ChemSusChem 2 (2009) 672–675.

[24] T.S. Hansen, I. Sadaba, E.J. Garcia-Suarez, A. Riisager, Cu catalyzed oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran and 2,5-furandicarboxylic acid under benign reaction conditions, Appl. Catal., A 456 (2013) 44–50.

[25] S.G. Wang, Z.H. Zhang, B. Liu, Catalytic conversion of fructose and 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid over a recyclable $Fe_3O_4CoO_x$ magnetite nanocatalyst, ACS Sustainable Chem. Eng. (2015), http://dx.doi.org/10.1021/sc500702q.

[26] J.T. Groves, T.E. Nemo, R.S. Myers, Hydroxylation and epoxidation catalyzed by iron-porphine complexes. Oxygen transfer from iodosylbenzene, J. Am. Chem. Soc. 101 (1979) 1032–1033.

[27] C.M. Che, V.K.Y. Lo, C.Y. Zhou, J.S. Huang, Selective functionalisation of saturated C–H bonds with metalloporphyrin catalysts, Chem. Soc. Rev. 40 (2011) 1950–1975.

[28] C.P. Du, Z.K. Li, X.M. Wen, M.X.J. Wu, X.Q. Yu, M. Yang, R.G. Xie, Highly diastereoselective epoxidation of cholest-5-ene derivatives catalyzed by polymer-supported manganese(III) porphyrins, J. Mol. Catal. A: Chem. 216 (2004) 7–12.

[29] T. Hashimoto, Y.K. Choe, H. Nakano, K. Hirao, Theoretical study of the Q and B bands of free-base, magnesium, and zinc porphyrins, and their derivatives, J. Phys. Chem. A 103 (1999) 1894–1904.

[30] W. Nam, H.J. Kim, S.H. Kim, R.Y.N. Ho, J.S. Valentine, Metal complex-catalyzed epoxidation of olefins by dioxygen with Co-oxidation of aldehydes. A mechanistic study, Inorg. Chem. 35 (1996) 1045–1049.

[31] R.R. Sever, T.W. Root, DFT Study of solvent coordination effects on titanium-based epoxidation catalysts. Part one: formation of the titanium hydroperoxo intermediate, J. Phys. Chem. B 107 (2003) 4080–4089.