Catalytic Aerobic Oxidation of Biomass-based Furfural into Maleic Acid in Aqueous Phase with Metalloporphyrin Catalysts

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Catalytic oxidation of renewable furfural into valuable maleic acid in aqueous solutions using metalloporphyrin catalysts was investigated for the first time. The synthesized catalysts were characterized by FT-IR, UV–vis, ¹H NMR, elemental analysis, and TGA. The catalysts varied in metal active sites and functional groups, which had different effects on their catalytic activity. Furthermore, the effects of temperatures, reaction time, catalyst loading, and oxygen pressure were studied in detail. Maleic acid could be achieved in 44% yield by using FeT(p-Cl)PPCl as catalyst under optimal conditions. Finally, FeT(p-Cl)PPCl could be reused in five consecutive runs without a significant loss of activity.

Keywords: Furfural; Biomass catalytic conversion; Metalloporphyrins; Maleic acid.

INTRODUCTION

Since the problems of energy depletion and environmental pollution have intensified in the past decade, there is an urgent need to seek potential alternatives to feedstock based on nonrenewable fossil resources. Biomass, as the most abundant renewable resource, has drawn growing interest from people and been used as the starting material for the synthesis of chemical intermediates and fuels.¹⁻⁴ Furfural, a biomass-derived five-carbon product, originates from many agricultural materials that are not competitive with human needs (e.g. wheat, corncobs, sawdust) and could be synthesized to maleic acid and other important platform chemicals.^{5,6} Maleic acid is a key downstream product because of its high applied value in polyester resins, surface coatings, lubricant additives, plasticizers, agrochemicals, and pharmaceuticals.^{7,8} But it is still manufactured from aerobic oxidation of petroleum-based n-butane or benzene under difficult conditions in the industry,^{9,10} which can hardly decrease the consumption of energy or improve economy. Thus, efforts are needed to convert the pathway of producing maleic acid and its derivatives from petroleum-based resources to biomass-based resources.

In 2011, the route to produce maleic acid from renewable furfural was first reported. Copper and iron salts displayed potential catalytic activity to the reaction, and the combination of copper nitrate with phosphomolybdic acid achieved a yield of 49.2% maleic acid under 2 MPa O₂ pressure after 14 h of reaction.¹¹ Later. Guo et al.¹² developed a new strategy for the aerobic oxidation of furfural to maleic acid in an aqueous/organic biphase system with improved product selectivity, and explored the product separation and reactant recycle. A yield of 34.5% maleic acid with 68.6% selectivity was achieved in a water/tetrachloroethane biphase system (v/v, 2:0.8) with a phosphomolybdic catalyst. Lan et al.13 described the transformation of furfural into maleic anhydride over H₅PV₂Mo₁₀O₄₀ mixed with Cu(CF₃SO₃)₂ and obtained a vield of 54% maleic anhydride under optimized conditions. Besides molecular oxygen, hydrogen peroxide was also employed as an oxidant to catalyze the oxidation of furfural.¹⁴ Titanium silicalite was used as the catalyst. As for the reaction mechanism, the route of furfural oxidation to maleic acid might involve epoxidation and rearrangement. Very recently, Li et al.15 demonstrated a heterogeneous catalytic system of Mo-V oxides as

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catalysts for the production of maleic anhydride from furfural, and reached a yield of 65% over the Mo–V–O catalyst (Mo/V, 4:1) under optimal conditions, and the catalyst could be recycled more than three times. The use of other biomass substrates generated a yield of 71% maleic anhydride from levulinic acid¹⁶ with supported vanadium oxides, and 5-hydroxymethyl furfural (5-HMF)^{17,18} was also employed over the corresponding catalysts.

All the studies above were devoted to developing a new route for producing maleic acid from biomass materials and for replacing the current industrial fossil fuel routes, bringing out much progress. Nevertheless, further efforts are needed to improve the reaction conditions under high oxygen pressure (2 MPa or higher) and long reaction time, and to expand the use of catalysts beyond phosphomolybdic acid type or V-based mostly. As the biomimetic models of cytochrome P450, metalloporphyrin (MP) catalysts exhibit efficient activity for many oxidation reactions of organic compounds under mild conditions, such as alkanes,¹⁹ cycloalkanes,^{20,21} alkenes,²² alkylaromatics,^{23,24} and alcohols.^{25,26} A few studies also reported the oxidation of carbohydrates 5-HMF^{27,28} over supported MPs. However, to the best of our knowledge, there is no investigation on the oxidation of furfural to maleic acid using MPs as catalysts.

In this work, the catalytic performance of MPs for the oxidation of furfural to maleic acid in aqueous solutions was studied (Equation 1). The optimum reaction conditions were also investigated, including the reaction temperature, reaction time, catalyst loading, and oxygen pressure. Additionally, the catalysts were characterized via Fourier transform infrared (FT-IR), UV–vis, ¹H NMR, elemental analysis (EA), and thermogravimetric analysis (TGA). It is hoped that metalloporphyrins will be widely employed in the field of biomass materials catalysis.



RESULTS AND DISCUSSION Characterization of catalysts

Figure 1 shows the FT-IR spectra of 5,10,15,20tetraphenylporphyrin (TPP), T(p-Cl)PP, T(p-CH₃)PP, Na₄TSPP, and FeTPPCI. The main characteristic Huang et al.



(c) T(p-Cl)PP, (d) Na₄TSPP, and (e) T(p-CH₃)PP.

absorption bands of TPP, T(p-Cl)PP, and T(p-CH₃)PP are roughly similar. The band at about 3317 cm^{-1} is attributed to the stretching vibration of N-H, and the bands near 960 cm^{-1} are related to the bending vibrations of N–H. The bands in the region $3060-2900 \text{ cm}^{-1}$ are assigned to the stretching vibration of C-H of porphyrins. The band at about 1344 cm^{-1} represents the vibration of C=N in pyrrole rings. Moreover, the strong absorption bands at around 798 and 698 $\rm cm^{-1}$ are attributed to the skeletal vibration of the porphyrin rings. In the spectrum of Na_4 TSPP, the bands at 1192 and 1040 cm⁻¹ represent the stretching vibration of S=O of sulfonate, indicating that the porphyrin had been sulfonated. After the metalation reaction (e.g. FeTPPCl in Figure 1), new sharp absorption bands appear at approximately 998 cm⁻¹, which are due to the vibration of N-metal bonds. For other metal tetraphenylporphyrins, the N-metal absorption bands tend to shift to lower wavenumbers with the increase of the atomic number. In addition, due to the coordination of M²⁺, the vibrations of N-H at around 3317 and 960 cm⁻¹ disappear, which indicates the successful insertion of the metal ions into free-base porphyrins.

Figure 2 presents the UV-vis spectral results of TPP and FeTPPCl in the range 700–300 nm. The spectra of TPP shows one intense Soret band at 417 nm generated by the transition from $a_{1u}(\pi)$ to $eg^*(\pi)$ and four less intense Q bands in the 650–510 nm region



Fig. 2. UV-vis spectra of TPP and FeTPPC1 at room temperature in dichloromethane solution.

induced by the $a_{2u}(\pi) - eg^*(\pi)$ transitions.²⁹ After metalation, the Soret band of metal porphyrins slightly shifts (red, or in case of FeTPPCl blue), and the peaks of the Q bands are fewer compared to free-base porphyrins because of the increased molecular symmetry,³⁰ which are important signs indicating the formation of MPs. Other porphyrin ligands and their metal complexes show similar characteristics as TPP and FeTPPCl.

The EA of the MPs used in catalytic experiments was performed. The results [in the electrospray ionization (ESI) mode] show that the experimental values are basically consistent with the calculated ones.

Thermogravimetry/differential thermogravimetry (TGA/DTG) analysis of FeT(p-Cl)PPCl was carried out



Fig. 3. TG/DTG curves of FeT(p-Cl)PPCl.

under a N₂ atmosphere. As shown in Figure 3, a weight loss of 4.28% within 358-415°C is attributed to the dissociation of axial chloride of the complex. A significant weight loss (12.22%) within 415-520°C is caused by the decomposition of porphyrin rings. Clearly, the FeT(p-Cl)PPCl catalyst is stable up to 358°C.

Catalytic oxidation of furfural into maleic acid with different MP catalysts

Metallic properties of catalysts often play a decisive role in most oxidation reactions of organic compounds,³¹ including furfural. Only 30% of substrate converted as a result of the polymerization and little maleic acid could be detected when no catalyst was added to the reaction system (Table 1, entry 1), which confirms that the oxidation reaction to maleic acid hardly occurs without any catalyst. In order to identify the potential catalyst, we synthesized a series of metal tetraphenylporphyrins and used them in the reactions (Table 1 entries 2-7). As reported, copper-based salts are the most potential catalysts for the oxidation of furfural into maleic acid.¹¹ However, in this reaction system, CuTPP displayed poor catalytic activity and produced only 1.9% maleic acid (Table 1, entry 2). In comparison. ZnTPP improved the catalytic efficiency slightly and gave a yield of 8.6% maleic acid and a conversion of 37.7% furfural, while CoTPP generated a 3.4% yield of maleic acid and a 26.5% conversion of furfural. FeTPPCl gave a yield of 20.4% maleic acid and a conversion of 47.8% furfural under the same conditions, indicating that FeTPPCl has the highest catalytic activity for the oxidation of furfural to maleic acid among these metal porphyrins. Thus, iron-based MP was the most effective catalyst in this system. The other metal teraphenylporphyrins (MnTPPCl, NiTPP) showed little catalytic efficiency for the reaction and were not considered potential catalysts.

The following work was conducted to study the impact that the different functional groups on iron porphyrins made on the target reaction. Thus, the same mole of FeT(p-Cl)PPCl and FeT(p-CH₃)PPCl was used in the furfural oxidation reaction, including the electron-withdrawing group -Cl and the electrondonating group -- CH₃, respectively. FeTSPPCl containing the water-soluble substituent -SO₃Na on the porphyrin macrocycle was also investigated as a comparison. Differences in the activity of these iron-

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Entry	Catalyst	Conversion (%)	Yield (%)	Selectivity (%)
1	_	29.7	0.6	2
2	CuTPP	28.4	1.9	6.9
3	ZnTPP	37.7	8.6	22.7
4	CoTPP	26.5	3.4	12.6
5	MnTPPCl	24.6	0.3	1.3
6	NiTPP	25.9	0.4	1.6
7	FeTPPCl	47.8	20.4	42.7
8	FeT(p-CH ₃)PPCl	43.6	26.3	60.3
9	FeT(p-Cl)PPCl	49.6	33	66.7
10	FeTSPPCl	49.3	25.2	51.1
11	FeSO ₄	45.5	18.5	40.7
12	FeCl ₃	41.2	13.4	32.5
13	Fe(NO ₃) ₃	35.2	11.1	31.5

Table 1. Conversion furfural into maleic acid over different metalloporphyrins and iron salts^a

^a Reaction conditions: catalyst, 3×10^{-5} mol; furfural,

2.5 mmol; H₂O, 4 mL; temperature, 90°C; 6 h; O₂, 1 Mpa.

based porphyrins with substituents could be observed and the reactivity followed the following order: FeTPPCl < FeTSPPCl \approx FeT(p-CH₃)PPCl < FeT(p-

Cl)PPCl. It is interesting that the yield of maleic acid could be improved compared with FeTPPCl depending on whether the iron porphyrins contained an electronwithdrawing or electron-donating group. The possible reason is that the introduction of substituents provided the steric effects necessary to reduce the oxidative degradation of porphyrins, which enhanced the stability of the catalysts.³² The catalytic activity of iron salts (entries 11-13) was also investigated in the experiment. The different iron salts displayed some activity to the reaction, but it was relatively low compared to that of iron porphyrins, indicating that the large π -conjugated structure of porphyrin ligands could improve the catalytic performance of the metal sites. FeT(p-Cl)PPCl showed a yield of 33% maleic acid and a conversion of 50% furfural under the reaction conditions, which indicated the best catalytic efficiency in this system. Therefore, FeT(p-Cl)PPCl was chosen and used in the following optimization of the reaction conditions.

Catalytic oxidation of furfural at different temperatures

The reaction temperature has a significant effect on furfural oxidation. As shown in Figure 4, both the yield and selectivity of maleic acid are nearly 0% below 70° C, indicating that the oxidation reaction of furfural



Fig. 4. Influence of the reaction temperature on the oxidation of furfural to maleic acid. Reaction conditions: FeT(p-Cl)PPCl, 20 mg; furfural, 2.5 mmol; H₂O, 4 mL; 6 h; O₂, 1 MPa.

to maleic acid could hardly occur. The yield of maleic acid increased from 6.1% at 70°C to 21.9% at 90°C. Then, the yield of maleic acid rose slightly with the temperature and reached 27.5% at 110°C. However, the selectivity of maleic acid, which increased sharply from 70 to 90°C, began to decrease, reaching a maximum (47.9%) at 90°C. This may be attributed to the dominant side reaction of polymerization of furfural, with the appearance of a black precipitate clearly after the reaction. A higher reaction temperature would benefit the conversion of furfural at all times, because with the temperature rising from 60 to 110°C, it still maintains furfural catalytic conversion efficiency to maleic acid over FeT(p-Cl)PPCl when above 90°C, but the selectivity of the side product becomes dominant in the system. Thus, 90°C is taken the best reaction temperature.

Time course of the oxidation of furfural into maleic acid

The effect of the reaction time is shown in Figure 5. The conversion of furfural gradually increases with prolonged reaction time. After 12 h of reaction, the conversion of furfural with FeT(p-Cl)PPCl is 87.6%. Similar to the trend in conversion, the yield of maleic acid rises slowly in the first 10 h and reaches a maximum at 10 h to 30.3%. The yield then decreases with longer reaction times, probably because of the product degrading to

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Fig. 5. Effect of the reaction time on the oxidation of furfural to maleic acid. Reaction conditions: FeT(p-Cl)PPCl, 20 mg; furfural, 2.5 mmol; H₂O, 4 mL; temperature, 90°C; O₂, 1 MPa.

small molecules.¹⁵ The selectivity of maleic acid increases at the beginning and reaches a maximum at 6 h to 47.9%, but it decreases slowly beyond 6 h, suggesting that the competitive side reaction becomes slightly more serious with longer reaction times.

Effect of catalyst loading on the aerobic oxidation of furfural to maleic acid

The effect of the catalyst amount is illustrated in Figure 6. As described above, maleic acid could be hardly produced without a catalyst in the reaction system. Both furfural conversion and maleic acid yield increase gradually with the increase of catalyst loading at first, supporting the hypothesis that increasing the number of active sites of the catalyst could support furfural oxidation. When 40 mg of FeT(p-Cl)PPCl was used, the yield (40.3%) and conversion (86.3%) reached a maximum. With further increase of the catalyst loading, the yield and conversion declined slowly, suggesting that excessive loading could hinder the reaction. The possible reason is that more byproducts cause interactions and thus reduce the effect of the catalyst. The selectivity of maleic acid also reached a maximum (47.4%) at the load of 30 mg of FeT(p-Cl)PPCl.



Fig. 6. Effect of different amounts of FeT(p-Cl)PPCl on furfural oxidation. Reaction conditions: furfural, 2.5 mmol; H₂O, 4 mL; temperature, 90°C; 10 h; O₂, 1 MPa.

Effect of oxygen pressure on the oxidation of furfural to maleic acid

The oxygen pressure also plays an important role in the reaction. As illustrated in Figure 7, higher oxygen pressure is favorable for furfural oxidation and



Fig. 7. Influence of the oxygen pressure on transformation of furfural to maleic acid. Reaction conditions: FeT(p-Cl)PPCl, 40 mg; furfural, 2.5 mmol; H₂O, 4 mL; temperature, 90°C; 10 h.

improves both the conversion and yield over FeT(p-Cl) PPCl, supporting that the increase of pressure favors the activation of oxygen and the generation of the catalytic product. A yield of 44% maleic acid could be achieved under 1.2 MPa. With further increase of pressure, the yield only slightly changed, while nearly full furfural conversion (98%) was obtained under 1.5 MPa. It is interesting that the oxidant pressure employed to produce maleic acid from furfural with iron porphyrins is lower than that reported in the literature.^{11,12}

Recycling of the FeT(p-Cl)PPCl catalyst

The reusability and stability of the FeT(p-Cl)PPCl catalyst were investigated for several cycles under the same conditions. After each run, the solid catalyst was separated by filtration, washed with hot water and ethanol, and dried in oven at 70°C overnight for the next cycle. The particle size of the catalysts in the system was measured by a granulometer, and the result showed that the average diameter of the catalyst was 1.7 µm. The test results are presented in Table 2. It could be seen that the yield of maleic acid remained constant at about 44% in the first four runs. The yield only decreased slightly (41.2%) after the fifth cycle. This may be because a small amount of the Fe (III) porphyrins were destroyed by O₂. In addition, no absorption bands of porphyrins were detected in the UV-vis spectra of the reaction solution after the tests, demonstrating that the catalysts remained insoluble throughout the experiments. Finally, the FT-IR and UV-vis spectra (see the ESI) of the recovered FeT(p-Cl)PPCl showed that the structure remained intact after five recycling steps, indicating that the catalyst has good catalytic stability (Scheme 1).

Table 2. Recycling experiments of the catalyst^a

46.4
46.4
45.4
45.8
44.3

^a Reaction conditions: FeT(p-Cl)PPCl, 40 mg; furfural, 2.5 mmol; H₂O, 4 mL; temperature, 90°C; 10 h; O₂, 1.2 MPa.



M= Fe; R= H, Cl, CH₃, SO₃Na; L= Cl M= Mn; R= H; L= Cl M= Co, Ni, Cu, Zn; R= H

Scheme 1. Molecular structure of prepared porphyrin catalysts.

EXPERIMENTAL

Materials and methods

Pyrrole, benzaldehyde, salicylic acid, furfural, xylene, metal salts, propionic acid, and other solvents were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) 4-Chlorobenzaldehyde was provided by Shanghai Aladdin Industrial Inc. 4-Methyl benzaldehyde was obtained from Energy Chemical Reagent Co. Ltd. (Shanghai, China) FT-IR spectra were measured with a Nicolet 360 FT-IR instrument (Madison, Wisconsin, USA) (KBr disks) in the 4000–500 cm^{-1} region. UV-vis spectra were obtained using a TU-1901 dual-beam UV-vis spectrophotometer (Beijing Purkinie General Instrument Co. Ltd., Beijing, China) over the 200-800 nm range. ¹H NMR spectra were recorded in D₂O or CDCl₃ with a Bruker DPX 300 spectrometer (Billerica, MA, USA). Elemental analysis was obtained with a Vario EL III CHNS instrument (Hanau, Germany). Particle size of the catalysts was recorded using a ZetaPALS granulometer (New York, USA). TGA analvsis was performed on a STA409 instrument (Mettler Toledo International Trading Co. Ltd., Shanghai, China) at a heating rate of 20°C/min from 25 to 800°C.

Catalyst preparation

Meso-tetraphenylporphyrin, meso-tetrakis(4-chlorophenyl)porphyrin, and meso-tetrakis(4-methyl)porphyrin were prepared by the method of Adler with some

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changes.³³ Meso-tetrakis(4-sulfophenyl)porphyrin was prepared by a reported procedure.³⁴

Synthesis of 5,10,15,20-tetraphenylporphyrin (TPP)

In a 100-mL flask with three necks, 0.9 g of salicylic acid as an acidic catalyst was added into 30 mL of xylene mixed with benzaldehyde (1.272 g, 0.012 mol). The resulting mixture was heated at reflux temperature under magnetic stirring. Then a xylene solution (6 mL) of fresh distilled pyrrole (0.804 g, 0.012 mol) was added dropwise to the mixture for 10 min. After 3 h of reaction, the system was cooled down to room temperature. Then 15 mL of ethyl alcohol was added, and the mixed solution was placed in a refrigerator for 24 h. After filtering, the precipitate was washed several times with ethyl alcohol. The purple crude product was dried in vacuum overnight and purified by a chromatographic column using neutral alumina (100–200 mesh size) with dichloromethane as eluent.

Synthesis of metal tetraphenylporphyrins (MTPP)

In a typical experiment, 0.16 g of the tetraphenylporphyrin synthesized above was dissolved in DMF (30 mL). The mixture was heated under magnetic stirring. Then FeCl₂·4H₂O (five times the molar quantity of TPP) was added into the solution in batches at reflux temperature. After 4 h of reaction, the solvent was removed by distillation, and hydrochloric acid was added slowly until the brown solid on the reactor wall dissolved. The mixture was immersed in deionized water for 6 h. Then the product was filtered and washed with hydrochloric acid and water, and dried unde vacuum overnight. Other metal complexes were synthesized with $Zn(OAc)_2 \cdot 2H_2O$, $Cu(OAc)_2 \cdot H_2O$, CoCl₂·6H₂O, MnCl₂·4H₂O, and Ni(OAc)₂·4H₂O, respectively.

Synthesis of 5,10,15,20-tetrakis(4-chlorophenyl) porphyrin (T(p-Cl)PP) and 5,10,15,20-tetrakis(4-methyl) porphyrin (T(p-CH₃)PP)

The meso-substituted porphyrins T(p-Cl)PP and T(p-CH₃)PP were prepared using a similar method as TPP. A propionic acid solution (5 mL) of freshly distilled pyrrole (1.005 g, 0.015 mol) were added dropwise to the mixed solution of propionic acid (30 mL) and 4-chlorobenzaldehyde or 4-methyl benzaldehyde (0.015 mol) at reflux temperature under magnetic stirring for 1 h. After the reaction, the precipitate was filtered and washed with hot water and ethyl alcohol. The

crude product was purified via column chromatography using neutral alumina (100–200 mesh size) with chloroform as eluent.

Synthesis of 5,10,15,20-tetrakis(4-sulfophenyl)porphyrin (Na₄TSPP)

TPP (0.15 g) was added into a round-bottom flask with 3 mL of H_2SO_4 (98%), and then the mixture was heated at 100°C with magnetic stirring. After 6 h of reaction, the mixture was cooled down to room temperature and poured into 20 mL of ice water carefully. A solution of saturated sodium hydroxide was added dropwise until the PH was 8–9 and the color of solution turned from green to red. The solution was concentrated to about 10 mL, and added with hot methanol. Then the mixed solution was filtered immediately to remove Na₂SO₄, and the filter cake was washed with hot methanol until it became colorless. Finally, the filtrate was dried by a rotary evaporator.

Synthesis of meso-substituted iron (III) porphyrins

The meso-substituted iron (III) porphyrins FeT(p-Cl)PPCl, FeT(p-CH₃)PPCl, and FeTSPPCl were synthesized using the same method as FeTPPCl.

Catalytic experiments and analysis

In a typical reaction, a certain amount of catalyst was added to 4 mL of water in a PTFE container; then the furfural (0.242 g, 2.5 mmol) substrate was dissolved in the mixture. The container was placed in a 100-mL stainless autoclave charged with a certain pressure of oxygen. The reaction mixture was magnetically stirred at the desired temperature and then it was charged with a specific pressure of oxygen. After the reaction, the autoclave was cooled down to room temperature and depressurized carefully to atmosphere pressure. A certain amount of reaction mixture was diluted 100 times with deionized water as sample and quantitatively analyzed using an Agilent 1100 HPLC chromatograph (Santa Clara, CA, USA) equipped with a refractive index detector and a Bio-Rad Aminex HPX-87H (Shanghai, China) column (300 mm × 7.8 mm). A 0.005 M H₂SO₄ solution was employed as the eluent phase at 313 K and 0.55 mL/min flow rate. The main product after the reactions was separated by crystallization and identified by ¹H NMR and ¹³C NMR techniques (in the ESI mode). The amount of maleic acid and furfural was determined using the external standard

method. The conversion of furfural as well as the yield and the selectivity of maleic acid were calculated as follows:

Furfural conversion (mol%) =

(1–(moles of remaining furfural)

/(starting moles of furfural)) $\times 100\%$

Maleic acid yield (mol%) =

 $((moles of maleic acid)/(starting moles of furfural)) \times 100\%$

Maleic acid selectivity (mol%) =

((moles of maleic acid)/(starting moles of furfural

- moles of remaining furfural $)) \times 100\%$

CONCLUSIONS

The route of producing maleic acid from renewable furfural over MP catalysts was investigated for the first time. The types of metal sites determined the catalytic activity of porphyrins during the furfural oxidation reaction. FeTPPCl was found to be the most active catalyst. The peripheral substituents in MPs also had a remarkable impact on the catalytic activity. FeT(p-Cl)PPCl, which contains electron-attracting group (-Cl), exhibited the best catalytic efficiency to the reaction. FeT(p-Cl)PPCl produced a yield of 44% maleic acid with the load of 40 mg at 90°C for reaction of 10 h under 1.2 MPa oxygen pressure. Moreover, recyclability experiments showed that the FeT(p-Cl)PPCl catalyst could be reused in five recycles without any significant decrease in the catalytic performance. We studied the application of MPs in the field of catalytic conversion of biomass and demonstrated that MPs exhibited good catalytic activity in furfural oxidation under milder conditions. Further works on supported MPs to be used in the reaction are going on.

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Suporting information

Additional supporting information is available in the online version of this article.

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