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Iron-based metalloporphyrins as efficient catalysts for aerobic oxidation of biomass derived furfural into maleic acid



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ARTICLE INFO	A B S T R A C T
<i>Keywords:</i> Iron porphyrins Supported catalysts Biomass Furfural	A series of porphyrin type catalysts with the metal active sites of Fe were prepared and investigated in aerobic ovidation of biomass based furfural to maleic acid (MAD) in aqueous phase. The catalytic performance of meso-
	tetrakis(4-bromophenyl)porphyrin iron (III) chloride (FeT(<i>p</i> -Br)PPCl) immobilized on different supports was evaluated. It was interesting to find that the catalytic activity varied with the supports and followed the trend:
	FeT(p-Br)PPCl/SBA-15 > FeT(p-Br)PPCl/meso-ZSM-5 > FeT(p-Br)PPCl/MCM-41. The effect of reaction con- ditions were discussed in detail over $FeT(p-Br)PPCl/SBA-15$ catalyst, and 56.1% yield and 73.8% selectivity of MAD were obtained from renewable furfural under the optimal conditions. Moreover, the $FeT(p-Br)PPCl/SBA-15$

catalyst could be reused five times without a significant decrease of activity in recycling examinations.

1. Introduction

As the biomimetic models of the cytochrome P-450 monooxygenase enzyme, metalloporphyrins have been extensively studied in the past decades for their efficient catalytic ability in hydroxylation and epoxidation reactions of hydrocarbons [1-4]. Many reactions are performed with metalloporphyrins under mild conditions due to the inherent properties of these models. However, metalloporphyrins employed as catalysts in homogeneous reaction systems have several drawbacks. For instance, they are not stable enough due to the aggregation of porphyrin rings caused by π - π interaction [5], and it's difficult to realize the recovery of these expensive catalysts from the homogeneous media at the end of the reaction, which limit the practical applications of them in industrial production. To overcome the disadvantages, immobilization of metalloporphyrin complexes on suitable and stable supports is an effective method. A great deal of attempts towards the immobilization of metalloporphyrins on various supports including silica, zeolite, porous glass, chitosan and resins have been investigated [6–10]. In comparison with homogeneous porphyrins, immobilized porphyrins exhibit higher stability and can be easily separated from the heterogeneous system for the next use. Furthermore, the special structure of supports provide a better microenvironment for the substrates to interact with the active sites of catalysts, which not only keep the high catalytic activity of metalloporphyrins, but also enhance the selectivity of the target products [11].

Supported metalloporphyrin catalysts show a good application prospect in oxidation of organic compounds, but only a few studies referred to the utilization of them in oxidation of biomass materials, which are the most abundant renewable resources on the earth [12,13]. As the potential alternative feedstock of traditional fossil resources, biomass can be used to produce many platform chemicals and fuel products [14-16]. Furfural is one of the biomass derived 5-carbon product and abundant in many agricultural materials such as wheat, corncobs and sawdust, which are not competitive with human beings. Thus, it's very attractive to convert furfural to value added products as the replacements of fossil-derived chemicals. In fact, more than 1600 commercial chemicals can be produced from furfural [17]. Compared with furfural, maleic acid (MAD) is currently a fossil-derived product, which can be manufactured from the route of aerobic oxidation of *n*butane or benzene under hard reaction conditions in industry [18]. MAD is a key downstream chemical for its high applied value in polyester resins, surface coatings, lubricant additives, plasticizers, agrochemicals, pharmaceuticals, etc [19]. From the view point of green chemistry, establishing the biomass-based MAD formation route by oxidation of renewable furfural over metalloporphyrin type catalysts under mild conditions is both environmental friendly and cost effective.

In this paper, different iron porphyrins were prepared. Meso-tetrakis (4-bromophenyl)porphyrin iron (III) chloride complex (FeT(*p*-Br)PPCl) was successfully immobilized on three different mesoporous materials: SBA-15, MCM-41 and *meso*-ZSM-5. We chose these three mesoporous

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Scheme 1. Oxidation of furfural to MAD catalyzed by iron-based metalloporphyrins.

materials mainly because they were common supports in supported catalysts, and each had different structural characteristics. These differences were exactly what we need in order to find the most suitable support for immobilized iron porphyrins. The catalysts synthesized were characterized by FT-IR, UV-vis, ¹HNMR, XRD, N₂-adsorption-desorption, SEM, TEM and TGA techniques. Both unsupported and supported porphyrin catalysts were used to catalytic the oxidation of furfural into MAD in the presence of dioxygen (1 MPa) in aqueous phase (Scheme 1). In addition, the effect of reaction parameters (reaction temperature, reaction time and catalyst amount) on the catalytic activity and the recycle tests of catalyst were also investigated in detail.

2. Experimental

2.1. Reagents and materials

Pyrrole, propionic acid, ferrous chloride tetrahydrate, furfural, ammonia (28 wt%), cetyltrimethylammonium bromide (CTAB) and tetraethyl orthosilicate (TEOS) were purchased from Sinopharm Chemical Reagent Co. Ltd.; Maleic acid, P123, tetraethyl ammonium hydroxide (TPAOH, wt%) and aluminum isopropoxide (AIP) were purchased from Shanghai Aladdin Industrial Inc.; Other main reagents used in the work were obtained from Energy Chemical Reagent Co. Ltd.

2.2. Catalyst preparation

2.2.1. Preparation of MCM-41

MCM-41 molecular sieves were prepared by the following literature procedures [20,21]. 1.37 g of CTAB was added into 50 mL of deionized water with gentle stirring at 40 °C. After a clear solution was formed, TEOS (5.2 mL) was added dropwise and aqueous ammonia was added until the pH of the mixed solution was adjusted to 10.5. With continued stirring for 3 h, the mixture was transferred to an autoclave equipped with a Teflon liner and heated at 105 °C for 24 h. Then the reaction was stopped and the gel was filtered, washed with deionized water and ethanol, dried in oven at 80 °C for 8 h. Finally, the solid was calcined at 550 °C for 6 h.

2.2.2. Preparation of SBA-15

SBA-15 mesoporous material was synthesized according to the method described in literature with a slight change [22]. In a typical synthesis, 4 g of P123 as organic template was dissolved in 30 mL of deionized water. After stirring at 42 °C for 1 h, 100 mL of HCl solution (2 M) was added. Then 8.5 g of TEOS was added dropwise and the resultant solution was stirred for 22 h, followed by hydrothermal treatment at 100 °C for 24 h. The solid product was collect by filtration, washed with deionized water and ethanol, dried in oven at 80 °C for 8 h, and then calcined at 550 °C for 6 h.

2.2.3. Preparation of meso-ZSM-5

We first synthesized microporous ZSM-5 zeolite according to the previous report [23]. The synthesis steps were as follows: 3 g of TEAOH as organic template was dissolved in 45 mL of deionized water, and then NaOH was added to the mixture followed by adding a measured amount of AIP as aluminum source. The mixed solution was stirred at room temperature for 1 h. Then 10.4 g of TEOS was added dropwise and the resultant solution (Si/Al = 60, molar ratio) was stirred for several hours. Subsequently, the mixture obtained was transferred to the Teflon-lined autoclave and crystallized by hydrothermal treatment at 170 °C for 72 h. Then the solid product was separated via filtration and washed with deionized water and ethanol, and dried at 80 °C for 8 h. Finally, the collected solid was calcined at 550 °C for 6 h to obtain ZSM-5. Meso-ZSM-5 was prepared by a simple alkaline treatment [24]. The obtained ZSM-5 was added to a 250 mL round-baker and then refluxed in a reflux condenser filled with a 0.5 M aqueous NaOH solution at 70 °C for 30 min. Then the solid zeolite was recovered by filtration, washing with deionized water, drying, and calcination in air at 300 °C for 5 h to obtain meso-ZSM-5.

2.2.4. Preparation of different porphyrin ligands

Porphyrin ligands were synthesized by the method of Alder with some modifications [25]. In a 100 mL of flask with three necks, 0.015 mol of corresponding benzaldehyde was dissolved in 30 mL of propionic acid solution. The mixture was heated at reflux temperature with vigorous stirring. Subsequently, 0.015 mol of freshly distilled pyrrole solved in propionic acid solution (5 mL) was slowly added into the above mixture. After a period of time of reaction, the mixture solution was cooled to room temperature and placed in the refrigerator overnight. Then the purple solid was filtered and washed with hot water and ethanol and dried at 80 $^{\circ}$ C for 8 h. The crude product was purified via column chromatography using neutral alumina (100–200 mesh size) with chloroform or dichloromethane as eluent.

2.2.5. Preparation of iron-based porphyrins

In a typical synthetic process, 0.16 g of porphyrin ligand synthesized above was dissolved in 30 mL of DMF. The mixed solution was heated at reflux temperature under magnetic stirring. Then $FeCl_2\cdot 4H_2O$ (four times the molar quantities of the ligand) was added into the solution in three batches. The reaction was carried out for 4 h and the solvent was removed by reduced pressure distillation, then hydrochloric acid was added slowly until the brown solid on the reactor wall was full dissolved. The mixture was immersed in deionized water overnight, collected via filtration and washing with hydrochloric acid and deionized water, and dried in oven at 80 °C for 8 h.

2.2.6. Preparation of supported feT(p-Br)PPCl catalysts

In a 100 mL round bottom flask, 0.5 g of support (MCM-41, SBA-15 and meso-ZSM-5) was dispersed in 15 mL of DMF. The mixture solution was heated to 120 °C with vigorous stirring. Then 0.1 g of FeT(p-Br) PPCl DMF solution were slowly added into the above mixture. After 24 h of reaction, the brown solid was filtered and exhaustively washed with solvent to remove the weakly adsorbed iron porphyrins.

2.3. Catalysts characterization

FT-IR spectra were measured with a Nicolet 360 FT-IR instrument (KBr discs) in the 4000–500 cm⁻¹ region. UV–vis spectra were obtained using a TU-1901 dual-beam UV–vis spectrophotometer over the 300–700 nm range. ¹H NMR spectra were recorded in CDCl₃ with a Bruker DPX 300 spectrometer. X-ray diffraction (XRD) patterns of samples were performed on a Bruker D8 Advance powder diffractometer with a Ni-filtered Cu/K α radiation source at 40 kV and 20 mA in the 2 θ range of 0.5–50° at the rate of 0.5° min⁻¹. The scanning electron microscope (SEM) images were taken on a HITACHI S-4800 emission scanning microscope. Transmission electron microscope

(TEM) images were obtained with a JEOL JEM model 2100 microscope operated at 200 kV. The Brunauer–Emmett–Teller (BET) surface areas were determined by N_2 adsorption–desorption measurements (Micromeritics ASAP 2020) at liquid N_2 temperature. Surface areas were calculated by using the BET method. Pore size distributions were calculated by the BJH model. Thermal gravimetric analysis (TGA) of samples were recorded on a STA409 instrument under a nitrogen atmosphere. The temperature was between 25 and 600 °C at a heating rate of 20 °C min⁻¹. The amount of iron on per gram of supports was determined by means of ICP-OES with an Optima 7300DV (PerkinElmer) spectrometer.

2.4. Catalytic test

The oxidation reaction was carried out in a 100 mL of autoclave reactor equipped with a magnetic stirrer. Typically, porphyrin catalysts and furfural mixed water were added into the autoclave reactor, and the reaction mixture was heated to the setting temperature with magnetic stirring at a speed of 500 rpm. Then the mixture was pressurized to 1 MPa of pressure with molecular oxygen. After a setting time of reaction, the autoclave reactor was cooled to room temperature and depressurized carefully to atmosphere pressure. The catalysts were separated by filtration and the sample was diluted with deionized water and analyzed by HPLC using an Agilent Alliance System instrument (1100 series), equipped with a refraction index detector and a Bio-Rad Aminex HPX-87H column (300 mm \times 7.8 mm). A 0.005 M H₂SO₄ solution was employed as the eluent phase at 313 K and a $0.55 \, \text{mL} \, \text{min}^{-1}$ flow rate. The main product (MAD) of the reaction was separated via crystallization and identified by FT-IR, ¹H NMR and ¹³C NMR techniques [in the Electronic Supporting Information (ESI)]. The conversion of furfural, the yield and the selectivity of MAD were determined using the external standard method.

3. Results and decision

3.1. Characterization of the catalysts

The FT-IR spectra of T(*p*-Br)PP, FeT(*p*-Br)PPCl, SBA-15 and FeT(*p*-Br)PPCl/SBA-15 were given in Fig. 1. The main features of porphyrins could be observed (Fig. 1A, B). The absorption bands at 3311 and 964 cm⁻¹ were attributed to the vibrations of N–H bonds. The peaks in the range of 3025–2854 cm⁻¹ were due to the stretching vibrations of



Fig. 1. FT-IR spectra of (A) T(*p*-Br)PP, (B) FeT(*p*-Br)PPCl, (C) SBA-15 and (D) FeT(*p*-Br)PPCl/SBA-15.



Fig. 2. UV–vis spectra of T(*p*-Br)PP and FeT(*p*-Br)PPCl at room temperature in dichloromethane solution.

C-H bonds. Meanwhile, the band at 1345 cm⁻¹ represented the vibration of C=N in pyrrole rings. After the metallation reaction, a new sharp absorption band at 997 cm^{-1} could be observed due to the vibration of N-Metal bond. In addition, the vibration of N-H at 3311 and 964 cm^{-1} disappeared. The sharp peak observed at 1086 cm^{-1} was assigned to the Si–O–Si stretching vibration (Fig. 1C). The broad band at 3425 cm⁻¹ could be attributed to stretching vibration of Si-OH groups and H–O–H of absorbed water. The weak band at 1656 cm⁻¹ corresponded to the bending vibration of the trapped water in the silica matrix. After the immobilization process, brown color was observed in FeT(*p*-Br)PPCl/SBA-15 catalyst, which indicated that FeT(*p*-Br)PPCl complexes had been successfully immobilized on the support. However, the main characteristic peaks of porphyrin complexes could not be clearly observed in Fig. 1D, the possible reason in that the complexes were highly dispersed on SBA-15 molecular sieves [26]. Other catalysts were also investigated by FT-IR spectroscopy (in the ESI).

Fig. 2 depicted the UV–vis results of T(p-Br)PP and FeT(p-Br)PPCl. In the spectrum of T(p-Br)PP, one intense Soret band at 419 nm accompanied by four less intense Q-bands in the 510–650 nm region could be observed. After coordination with Fe^{2+} , the Soret band of porphyrin had a minor degree of blue shift. In addition, the peaks of Q-bands were relatively fewer compared to T(p-Br)PP due to the increased symmetry of molecule structure [27]. The decrease of the number of absorption peaks in the Q-band and the displacement of the Soret band were important signs of the formation of metal complexes, indicating that the metal ions were successfully coordinated to the porphyrin ligands. Other UV spectrums of porphyrin ligands exhibited the similar features (in Figs. S14–19).

The textural properties of both supports and catalysts were determined via N_2 adsorption-desorption analyses (Fig. 3 and Table 1). As shown in Fig. 3, all samples displayed type IV isotherm according to the classification of IUPAC. For MCM-41, a capillary condensation was evidenced in the P/P_0 range of 0.3–0.4, while the adsorption isotherms of SBA-15 and meso-ZSM-5 exhibited H1 and H4 hysteresis loop respectively, reflecting the microstructure difference of the three mesoporous materials. No significant differences between the isotherms of pure supports and supported metalloporphyrins were observed, indicating that the catalysts basically maintained the porous features of the supports. The surface areas, pore volumes, pore sizes and porphyrin loadings of samples were summarized in Table 1. It was clear that MCM-41 and SBA-15 exhibited a larger surface area and pore size, while the specific surface area of meso-ZSM-5 was relatively small



Fig. 3. Nitrogen adsorption-desorption isotherms of samples: (A) MCM-41 and FeT(*p*-Br)PPCl/MCM-41, (B) SBA-15 and FeT(*p*-Br)PPCl/SBA-15, (C) meso-ZSM-5 and FeT(*p*-Br)PPCl/meso-ZSM-5.

Table 1	
Physicochemical properties for supported catalysts.	

Entry	Sample	Surface area ^a ($m^2 g^{-1}$)	Pore volume ^b (cm ³ g ⁻¹)	Pore size ^c (nm)	Fe ^e (wt%)
1	MCM-41	947.4	1.136	4.63	-
2	FeT(p-Br)PPCl/ MCM-41	864.5	0.984	4.43	0.96
3	SBA-15	689.3	0.603	5.94	-
4	FeT(p-Br)PPCl/ SBA-15	473.2	0.495	5.84	0.83
5	Meso-ZSM-5	232.9	0.031	3.91	-
6	FeT(p-Br)PPCl/ meso-ZSM-5	90.8	0.019	3.70	0.63
7	FeT(p-Br)PP/ SBA-15 ^d	451.9	0.491	5.01	0.74

^a Surface areas were calculated by BET method.

^b Pore volumes were calculated by BJH method.

^c Pore sizes were calculated by BJH method.

^d The recovered FeT(p-Br)PP/SBA-15 catalyst after five times use.

^e The iron content of FeT(*p*-Br)PP/SBA-15 catalysts were determined by ICP-OES.

(Table 1, entries 1, 3, 5). Although the specific surface area of SBA-15 was smaller than that of MCM-41, the pore wall was thicker than MCM-41, resulting in better hydrothermal stability of SBA-15 than that of MCM-41 [22]. After the incorporation of iron porphyrins into supports, both surface areas and pore sizes showed a decreasing trend, which might be caused by the blockage of some pores [28]. It was well known that the specific surface area, pore size and hydrothermal stability for immobilized catalysts greatly affect the catalytic activity of the catalyst. In addition, the structural differences of different supports were also shown on the loading of iron porphyrin. In the metalloporphyrins/O2

system, iron porphyrins could combine with oxygen molecules to form the high-valent $PorFe^{IV} = O$ radical species, which was responsible for the oxidation activity of Fe-porphyins [29,30]. It was not difficult to find the iron content of FeT(p-Br)PP/meso-ZSM-5 catalyst was the lowest compared to FeT(p-Br)PPCI/SBA-15 and FeT(p-Br)PPCI/MCM-41 (Table 1, entries 2, 4, 6). Based on the above analysis, it could be inferred that the catalytic activity of FeT(p-Br)PPCI/SBA-15 was better than that of FeT(p-Br)PPCI/MCM-41 and FeT(p-Br)PPCI/meso-ZSM-5. These results were consistent with the experimental results (Table 1, entries 11–13), indicating that the nature of the supports had a significant effect on the activity of the catalysts.

The powder X-ray diffraction patterns for prepared catalysts were shown in Fig. 4. It could be found that SBA-15 (Fig. 4A) showed three typical diffraction peaks at 2θ values of 0.96, 1.56 and 1.82, corresponding to the reflections of (100), (110) and (200) planes respectively, indicating that SBA-15 was a well-ordered 2D hexagonal pore structure and micropores existed between mesopores and mesopores [31]. After the immobilization procedure, a lower intensity of reflection accompanying with a slight shifting of diffraction lines to higher angle in the (100) plane could be observed, suggesting that the introduction of porphyrin ligand had an effect on the crystallinity while the order mesoporous structure of SBA-15 remained almost unchanged. MCM-41 and FeT(p-Br)PPCl/MCM-41 (Fig. 4B) also displayed the typical characteristic peaks of 2D hexagonal materials, which was consistent with the typical patterns reported in the literatures [32]. However, reactants and products could only flow in two-dimensional pipelines and could not shuttled between pipelines. That was, the residence time of the reactants inside the FeT(p-Br)PPCl/MCM-41 was relatively short, and the contact with the FeT(p-Br)PPCl/MCM-41 was insufficient, resulting in a decrease in the activity of the FeT(p-Br)PPCl/MCM-41. The XRD patterns for meso-ZSM-5 (Fig. 4C) showed five distinct peaks at 2θ values of 7.92, 8.83, 23.01, 23.78 and 24.33, corresponding to the



Fig. 4. XRD patterns of (A) SBA-15 and FeT(p-Br)PPCl/SBA-15, (B) MCM-41 and FeT(p-Br)PPCl/MCM-41, (C) meso-ZSM-5 and FeT(p-Br)PPCl/meso-ZSM-5.

characteristics of MFI structure. In contrast, the significant decrease in the diffraction peak intensity of the FeT(p-Br)PPCl/meso-ZSM-5 compared to meso-ZSM-5 was due to the decrease of crystallinity after supported by porphyrins, which could also be seen from the results of SEM of FeT(p-Br)PPCl/meso-ZSM-5 and meso-ZSM-5.

The SEM analysis was carried out in order to investigate the

morphology of different samples. As shown in Fig. 5, the images of SBA-15 and MCM-41 particles showed sphere-like and bar-type structures respectively with a uniform size, while meso-ZSM-5 particles were similar to hexagon in nature. After incorporation of porphyrin complexes, the morphology structures of catalysts remained approximately constant. However, some particles of FeT(*p*-Br)PPCl/MCM-41 generated a



Fig. 5. SEM images of (A) SBA-15, (B) FeT(p-Br)PPCl/SBA-15, (C) MCM-41, (D) FeT(p-Br)PPCl/MCM-41 (E) meso-ZSM-5 and (F) FeT(p-Br)PPCl/meso-ZSM-5.



Fig. 6. TEM images of FeT(p-Br)PPCl/SBA-15 catalyst.

slight degree of aggregation, which was responsible for the severe decrease in catalyst activity. On the contrary, only some fine agglomerated sphere particles were observed on the surface of FeT(p-Br)PPCl/SBA-15 and FeT(p-Br)PPCl/meso-ZSM-5, which probably because the excess FeT(p-Br)PPCl complexes adhered to the outer surface of the supports during the immobilization process. The TEM images of FeT(p-Br)PPCl/SBA-15 catalyst (Fig. 6) from different angles witnessed a wellordered hexagonal arrangement of channels, which were consistent with the XRD results. From the degree of catalyst surface agglomeration, the surface structures of FeT(p-Br)PPCl/SBA-15 and FeT(p-Br)PPCl/meso-ZSM-5 were better than FeT(p-Br)PPCl/MCM-41, which was also an important parameter to measure the performance of a catalyst.

The TG/DTG analysis of FeT(*p*-Br)PPCl/SBA-15 was performed to determine the thermal stability of the catalysts. As presented in Fig. 7, the initial weight loss of 3.2% occured at the temperature range of 25–100 °C, which could be related to adsorbed water on the structure. The decomposition of porphyrin complex took place between 250 and 350 °C, corresponding to the weight loss of about 10.6% in Figure. Meanwhile, the peak of DTG curve demonstrated that the fastest weight loss of the catalyst appeared at about 310 °C. Therefore, it could be concluded that the FeT(*p*-Br)PPCl/SBA-15 catalyst was stable up to 250 °C.

3.2. Catalytic oxidation of furfural into MAD with different iron-based porphyrins

Firstly, a range of unsupported iron (III) porphyrins were employed in the catalytic experiments (Table 2, entries 1–7). All of them were active on the reaction, and the substituent groups on the porphyrin



Fig. 7. TG/DTG curves of FeT(*p*-Br)PP/SBA-15.

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Entry	Catalyst	Con ^b (%)	Y ^b (%)	S ^b (%)	C of Por ^b (mmol)
1	FeTPPCl	34.6	10.2	29.5	$7.4 imes 10^{-3}$
2	FeT(p-Cl)PPCl	36.8	15.4	41.8	$7.4 imes 10^{-3}$
3	FeT(p-Br)PPCl	47.7	19.7	41.3	$7.4 imes 10^{-3}$
4	FeT(o-F)PPCl	35.5	10.7	30.1	7.4×10^{-3}
5	FeT(p-CH ₃)PPCl	32.6	13.0	39.9	7.4×10^{-3}
6	FeT(p-OCH ₃)PPCl	37.7	14.2	37.7	7.4×10^{-3}
7	FeT(p-COOMe)PPCl	38.6	15.1	39.1	7.4×10^{-3}
8	MCM-41	37.8	1.5	4.0	0
9	SBA-15	35.7	2.9	18.1	0
10	Meso-ZSM-5	37.5	2.6	6.9	0
11	FeT(p-Br)PPCl/MCM-41	41.1	27.8	67.6	8.6×10^{-3c}
12	FeT(p-Br)PPCl/SBA-15	53.7	38	70.8	7.4×10^{-3c}
13	FeT(p-Br)PPCl/meso- ZSM-5	47.2	31.5	66.7	$5.6 imes 10^{-3c}$

 $^{\rm a}\,$ Reaction conditions: 3 mmol furfural; 50 mg catalyst; 6 mL H_2O; 90 °C; 6 h; 1 MPa O_2.

 $^{\rm b}$ Con = Conversion; Y = Yield; S = Selectivity; C of Por = Content of Porphyrin.

^c The amount of porphyrins on catalysts were calculated according to ICP-OES.

macrocycle have a remarkable impact on catalytic activity. The yield of MAD was improved in comparison with unsubstituted FeTPPCl depending on whatever types of anchoring groups they are. The reason was that the introduction of substituents provided the steric effects necessary to reduce the oxidative inactivation of porphyrins [33]. Additionally, the yield increased little (10.7%) with FeT(o-F)PPCl as catalyst. The introduction of the o-position substituents could lead to more displacement of Fe metal center, which had a negative effect on the reactivity [34]. The catalytic performance of different supported iron porphyrins was next investigated. It was evident that pure supports showed almost inactive in the reaction and only a small amount of substrates were converted due to the polymerization (Table 2, entries 8-10). In addition, it was known that MCM-41 and SBA-15 were neutral supports, while meso-ZSM-5 had a certain degree of acidity. However, the catalytic effects were very poor when three pure supports were used as catalysts for the reaction, indicating that the acidity of the catalysts did not play a role for converting furfural into maleic acid. Nevertheless, MAD yield increased sharply when three supported catalysts were used (Table 2, entries 11-13), indicating that the catalytic activity of the catalysts was related to the component of porphyrin complex. FeT(p-Br)PPCl/SBA-15 catalyst exhibited the best catalytic performance in three kinds of supported catalysts under the same reaction conditions, giving a conversion of 53.7% furfural and a selectivity of 70.8% MAD, suggesting that the special ordered channel structure of SBA-15 molecular sieves could be more favorable for the overall diffusion and transfer of furfural into MAD. Moreover, the catalytic results revealed that FeT(p-Br)PPCl/SBA-15 displayed much better catalytic behaviors than the unsupported porphyrins used in experiments, especially in



Fig. 8. Conversion of furfural to MAD over FeT(*p*-Br)PPCl/SBA-15 catalyst. Reaction conditions: 3 mmol furfural, 6 mL H₂O, 1 MPa O₂. (A) 50 mg FeT(*p*-Br)PPCl/SBA-15, 6 h. (B) 50 mg FeT(*p*-Br)PPCl/SBA-15; 100 °C. (C) 100 °C; 6 h.

selectivity respect (70.8%). Although FeT(*p*-Br)PPCl was the most active catalyst in all unsupported porphyrins, the selectivity of MAD was relatively poor (41.3%). Previous reports had demonstrated that high-valent PorFe^{IV} = O radical species formed by the combination of iron and oxygen molecules were the active sites for oxidation reactions [29,30]. Even though pure supports could hardly convert furfural into MAD in the reaction system, they provide a fine microenvironment where the oxidation reaction between furfural substrates and PorFe^{IV} = O active species could be performed more easily, enhancing the catalytic performance of porphyrins [35].

3.3. Effect of reaction conditions on the oxidation of furfural over feT(p-Br) PPCl/SBA-15

The effects of reaction conditions containing of reaction temperature, reaction time and catalysts loading were studied in detail over FeT(*p*-Br)PPCl/SBA-15 catalysts. The results were presented in Fig. 8. It was not difficult to find that the conversion of furfural increased with the temperature from 70 to 120 °C (Fig. 8A) and reached 81% at 120 °C. However, the maximum yield (48.3%) and selectivity (76.1%) of MAD were achieved at 100 °C. Afterward, the decrease in MAD yield and selectivity with increasing temperature from 100 °C to 120 °C was partly attributed to the oxidative degradation of MAD to other molecules. In addition, the side reaction (polymerization of furfural) was more likely to occur at higher temperatures, which was one of the reasons leading to a decrease in MAD yield. The effect of the reaction time was shown in Fig. 8B. The yield of MAD increased gradually in the first 6 h and reached a maximum (48.3%) at 6 h. Then the product began to decompose to small compounds as the yield presented a downtrend [36]. The selectivity of MAD maximized (79.5%) at 4 h and then decreased sharply, implying that the competitive side reaction became serious upon a prolonged reaction time. The effect of catalyst

amount on the reaction was also significant (Fig. 8C). The conversion of furfural and yield of MAD increased greatly with the catalyst amount at first, suggesting that increasing active sites of catalyst could benefit to the conversion of furfural into MAD. When 60 mg of FeT(*p*-Br)PPCl/SBA-15 was used, a yield of 56.1% MAD and a conversion of 76% furfural were obtained. However, both the conversion of furfural and yield of MAD decreased when the amount of FeT(*p*-Br)PPCl/SBA-15 was beyond 60 mg. These results demonstrated that the excessive amount of catalyst hindered the conversion of furfural into MAD. Thereform, 100 °C, 6 h and 60 mg FeT(*p*-Br)PPCl/SBA-15 were determined as the best reaction conditions.

3.4. Recycle of the feT(p-Br)PPCl/SBA-15 catalyst

The recyclability of FeT(*p*-Br)PPCl/SBA-15 was investigated under the optimal reaction conditions, and the results were shown in Fig. 9. As the heterogeneous reaction system, the catalyst could be easily separated by filtration, washed with hot water and ethanol, and dried in oven overnight after each run. It could be observed that the yield of MAD was almost unchanged (56%) in the first four runs and dropped a little in the fifth cycle. The BET (Table 1, entry 7) results of the recovered FeT(*p*-Br)PPCl/SBA-15 after five cycles reflected that more furfural polymers adsorb on the surface of catalyst, hindering the catalytic activity. Additionally, the small leaching of iron (from 0.83 wt% to 0.74 wt%) in the catalyst was also responsible for the slight loss of activity. In addition, the SEM and TEM (Fig. S20) characterizations of the recovered FeT(*p*-Br)PPCl/SBA-15 catalyst after five cycles showed that the structure remained intact, indicating that the catalyst has well catalytic stability.



Fig. 9. Reusability results of FeT(p-Br)PPCl/SBA-15 catalyst in conversion of furfural to MAD. Reaction conditions: 3 mmol furfural; 6 mL H₂O; 60 mg FeT(*p*-Br)PPCl/SBA-15; 1 MPa O₂; 100 °C; 6 h.

4. Conclusion

Iron-based metalloporphyrins as catalysts were investigated in oxidation of renewable furfural into MAD under mild reaction conditions. FeT(*p*-Br)PPCl was found that the catalyst with higher catalytic activity than other unsupported iron porphyrins. A comparison among different mesoporous materials (SBA-15, MCM-41 and meso-ZSM-5) as supports for supported metalloporphyrins catalysts was studied in detail. The supports with particular structures could create a microenvironment where the catalytic performance of porphyrin complexes was significantly improved, which was especially reflected in MAD selectivity aspect. FeT(p-Br)PPCl/SBA-15 catalyst exhibited the best catalytic performance in three kinds of supported catalysts, affording MAD in a yield of 56.1% and a selectivity of 73.8% at the furfural conversion of 76% under the optimal reaction conditions. Moreover, the recyclability experiments showed that the FeT(p-Br)PPCl/SBA-15 could be reused five times without a significant loss of activity, demonstrating a good stability of the catalyst. The well catalytic performance of FeT(p-Br) PPCl/SBA-15 suggested that supported metalloporphyrins could have a great potential to be applied in the field of biomass conversion.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2018.03.018.

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