

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

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ABSTRACT

A series of porphyrin type catalysts with the metal active sites of Fe were prepared and investigated in aerobic oxidation of biomass-based furfural to maleic acid (MAD) in aqueous phase. The catalytic performance of *meso*-tetrakis(4-bromophenyl)porphyrin iron (III) chloride (FeT(*p*-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 conditions 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

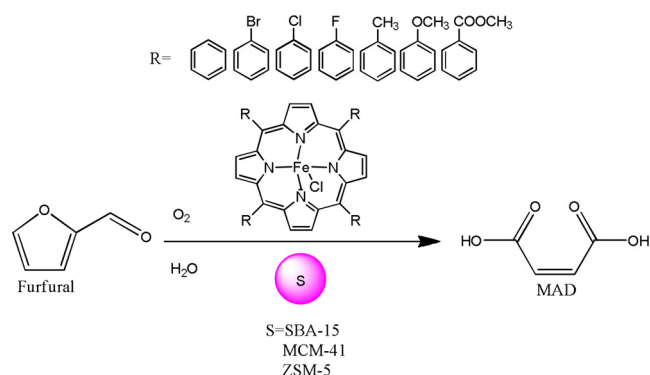
As the biomimetic models of the cytochrome P-450 monooxygenase enzyme, metalloporphyrins have been extensively studied in the past decades for their efficient catalytic ability in hydroxylation and epoxidation reactions of hydrocarbons [1–4]. Many reactions are performed with metalloporphyrins under 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, ^1H NMR, XRD, N_2 -adsorption-desorption, SEM, TEM and TGA techniques. Both unsupported and supported porphyrin catalysts were used to catalyze 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 collected 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 °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 $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (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 $\text{FeT}(p\text{-Br})\text{PPCl}$ 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 $\text{FeT}(p\text{-Br})\text{PPCl}$ 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 CDCl_3 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 $\text{Cu}/\text{K}\alpha$ radiation source at 40 kV and 20 mA in the 2θ 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

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