

Notes

Synthesis of Immobilized Catalysts by the Introduction of Iron(III) – Porphyrin into a Humic Acid via Ether – Linkages

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Abstract

To introduce 5,10,15,20-tetrakis(*p*-hydroxyphenyl)porphineiron(III) (FeTPP(OH)₄) into a humic acid (HA) via ether-linkages using an Williamson reaction, the carboxylic acid groups of phenolic acid moieties in the HA were masked by conversion to methyl esters. The resulting methyl esters of HA and FeTPP(OH)₄ were reacted in a DMF solution with 1,6-dibromohexane or 1,10-dibromodecane as spacer molecules in the presence of K₂CO₃, to produce two types of hybrid catalysts with different lengths of alkyl-chains in the linkages. Compared to an unmodified catalyst, FeTPP(OH)₄, the prepared catalysts were effective in retarding catalyst self-degradation and in enhancing PCP degradation.

Keywords: Iron(III)-porphyrin; Humic acid; Ether-linkage; Self-degradation; Catalytic oxidation; Pentachlorophenol

Introduction

Iron(III)-porphyrin complexes catalyze the oxidative degradation of chlorophenols (Shukla et al., 1996; Fukushima et al., 2007). However, a problem in using iron(III)-porphyrin is inactivation via self-degradation in the presence of oxygen donors, such as H₂O₂ and KHSO₅ (Smith, 1994; Fukushima and Tatsumi, 2006). In attempts to retard this self-degradation, metalloporphyrins can be incorporated into organic polymers via ether-linkages, in which the hydroxyl groups in meso-phenyl groups of metalloporphyrins are linked to phenolic hydroxyl groups in the polymers via a Williamson reaction (Uno et al., 1991).

Humic acid (HA) is a naturally occurring polyphenol that is found in the organic fraction of soil (Tan, 2003). Therefore, the possibility exists that iron(III)-porphyrins containing phenolic hydroxyl groups could be introduced into phenolic moieties in HAs via ether-linkages. However, the majority of phenol rings in HAs contain carboxylic acid groups (Del Rio and Hatcher, 1996). The presence

of carboxylic acids in phenol rings suppresses the ionization of hydroxy groups, which, in turn, inhibits the formation of ether-linkages that are produced using the Williamson reaction. To overcome this problem, the carboxyl groups can be converted into methyl esters (Gao et al., 2004). In the present study, the carboxylic acids in an HA sample were masked by conversion to methyl ester groups. An iron(III)-5,10,15,20-tetrakis(*p*-hydroxyphenyl) porphyrin (FeTPP(OH)₄) group was then incorporated into the phenolic hydroxyl groups in the HA via the formation of ether-linkages by reaction with dibromoalkanes, which serve as spacer molecules between FeTPP(OH)₄ and HA. In addition, the performance of the prepared catalysts was investigated, in terms of the kinetics of self-degradation and activity using the oxidation of pentachlorophenol (PCP) as a model reaction.

Materials and Methods

Materials

An HA sample was prepared from a Shinshinotsu

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peat soil sample using a method approved by the International Humic Substances Society (Swift, 1996). A sample of FeTPP(OH)₄ was prepared by refluxing a mixture of 5,10,15,20-tetrakis (*p*-hydroxyphenyl)-21*H*,23*H*-porphine and FeCl₂·4H₂O in DMF (Fukushima and Shigematsu, 2008). The methyl ester of HA (HA-Me) was prepared according to a method reported by Ikeya et al. (2006).

The HA-Me (25 mg, 0.1 mmol of phenolic hydroxyl groups) and FeTPP(OH)₄ (0.033 mmol) were placed in a round-bottom flask and the solids were then dissolved in DMF (100 mL). After adding K₂CO₃ (0.15 g), dibromoalkane in DMF (0.040 mmol) was added dropwise with vigorous stirring. After stirring for 2 days at room temperature, the DMF was removed, and 300 mL of a 5% aqueous solution of KOH was then added. After stirring for 1 day at room temperature, the solution was neutralized with aqueous H₂SO₄. After deionizing the solution by ultrafiltration and dialysis (1000 Da), the hybrid catalyst was freeze dried to give a powder. In the present study, 1,6-dibromohexane (E-6) and 1,10-dibromodecane (E-10) were used as spacer molecules between FeTPP(OH)₄ and HA-Me. To determine the extent of incorporation in the prepared catalysts, the iron content of the catalysts was determined by ICP-AES.

Characterization of catalysts

FTIR spectra were recorded using an FT/IR 600 type spectrometer (Japan Spectroscopic Co., Ltd.) with KBr pellets. The molecular weight distributions of HA-Me, E-6 and E-10 were characterized by means of a size exclusion chromatography (SEC), as described in a previous report (Fukushima et al., 2007). A TSK-Gel α-M column (7.8 mm i.d. × 300 mm) was employed for the separation. The void and total volumes for the column were 6.1 mL and 14.3 mL, respectively. Polystyrene sulfonic acid sodium salts were used to calibrate the molecular weights of HA-Me and the prepared catalysts. The eluent consisted of the mixture of 0.01 M phosphate buffer (pH 7) and acetonitrile. A 20 μL aliquot of sample (100

mg L⁻¹ in the eluent) was injected into a PU-980 type HPLC system (Japan Spectroscopic Co., Ltd.). The flow rate for the eluent was set at 1.0 mL min⁻¹, and the column temperature was maintained at 40°C. A UV-970 UV-vis detector (Japan Spectroscopic Co., Ltd.) was used for detection at a wavelength of 260 nm. To evaluate the kinetics of self-degradation of the catalysts, the decolorization of the catalysts was monitored at a detection wavelength of 425 nm using an RSP-1000-02-type stopped-flow spectroscopy system (Unisoku, Co., Ltd.).

Catalytic activity

A 2-mL aliquot of a 0.02 M Na₂HPO₄/ NaH₂PO₄/ citric acid buffer solution (pH 4 or 6) was placed in a 20-mL test tube. A 7.5-μL aliquot of 10 mM PCP in acetonitrile and a 50-μL aliquot of an aqueous catalyst solution (200 μM) were then added to the buffer solution. Subsequently, 0.1 M aqueous KHSO₅ (20 μL) was added, and the test tube was shaken at 25 ± 0.1°C. After a 60-min reaction period, 1 mL of 2-propanol was added to the solution. To determine the level of PCP in the test solution, a 20-μL aliquot was injected into a PU-980 type HPLC pumping system (Japan Spectroscopic Co., Ltd.). The conditions for the PCP analysis by HPLC have been described in a previous report (Fukushima et al., 2003). The concentrations of Cl⁻ in the reaction mixtures were determined by ion chromatography. The by-products produced by the PCP oxidation were identified by a GC/MS technique after extracting the reaction mixture (pH 4; [PCP]₀ 37.5 μM; [catalyst] 5 μM; [KHSO₅] 1 mM; reaction time 60 min at 25°C) with *n*-hexane (Fukushima et al., 2003). The assays for catalytic activity were conducted in triplicate runs, and the average values and their standard deviations were calculated.

Results and Discussion

Characterization of prepared catalysts

The elemental composition of HA, HA-Me and the prepared catalysts are summarized in Table 1. The

Table 1. Results of elemental analysis for HA, HA-Me, and the prepared catalysts.

| Compounds | %C | %H | %N | %O | %S | %ash | C/H | C/N |
|-----------|-------|------|------|-------|------|-------|------|------|
| HA | 54.52 | 5.35 | 2.17 | 35.08 | 0.66 | 2.22 | 0.86 | 29.3 |
| HA-Me | 60.64 | 6.35 | 1.77 | 28.22 | 1.30 | 1.72 | 0.80 | 40.0 |
| E-6 | 33.02 | 1.76 | 1.59 | 45.73 | 0.82 | 17.08 | 1.57 | 24.2 |
| E-10 | 55.82 | 4.76 | 3.36 | 29.47 | 1.10 | 5.49 | 0.98 | 19.4 |

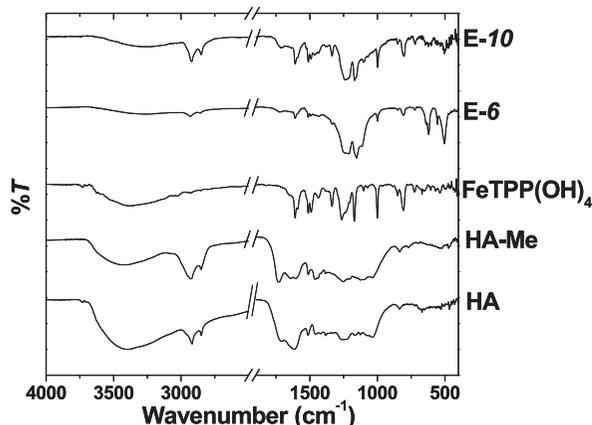


Fig. 1. FT-IR spectra of HA, HA-Me and the prepared catalysts.

C/N atomic ratios for E-6 and E-10 were much smaller than those for HA and HA-Me, suggesting that FeTPP(OH)₄, which contains nitrogen, was successfully introduced into the HA. Figure 1 shows FTIR spectra of HA, HA-Me and the prepared catalysts. For the spectrum of HA-Me, the peaks at 2940 and 2860 cm⁻¹, corresponding to C-H stretching of methyl groups were enhanced, compared to those for the original HA. In addition, the peak assigned to carbonyl C=O stretching at 1722 cm⁻¹ for the HA was shifted to a higher wavenumber, compared with that for HA-Me (1744 cm⁻¹). These results indicate that the carboxylic acids in the HA were, in fact, methylated, *i.e.*, converted into methyl ester groups. The following peaks were evident in the FeTPP(OH)₄ sample: at approximately 3470 cm⁻¹ (phenol O-H stretching); 1611 and 1516 cm⁻¹ (C=C ring stretching); 1476 cm⁻¹ (C=C stretching in porphyrin rings); 1338 cm⁻¹ (phenolic O-H bending); 1272 cm⁻¹ (phenolic C-O stretching); and, 1004 cm⁻¹ and 807 cm⁻¹ (out-of-plane C-H bending). Peaks corresponding to phenolic O-H stretching at 3470 cm⁻¹ were largely reduced in E-6 and E-10, compared to FeTPP(OH)₄. In addition, strong bands at 1240 and 1160 cm⁻¹, assigned to ether C-O stretching appeared in the spectra of E-6 and E-10, consistent with the formation of ether-linkages in phenolic hydroxyl groups of FeTPP(OH)₄. In addition, the bands corresponding to methylene C-H stretching (2870 and 2940 cm⁻¹) for E-10 were larger than those for E-6. This indicates that FeTPP(OH)₄ and HA are linked to one another via the methylene groups in the dibromoalkanes.

The iron contents of the prepared catalysts are

Table 2. Iron contents and half-lives ($t_{1/2}$) for the self-degradation for FeTPP(OH)₄ and the prepared catalysts.

| Catalysts | Fe content ($\mu\text{mol mg}^{-1}$) | $t_{1/2}$ (s) | |
|------------------------|---|---------------|-----------|
| | | pH 4 | pH 6 |
| FeTPP(OH) ₄ | 1.33 | 0.61±0.02 | 1.59±0.01 |
| E-6 | 0.18 | 1.60±0.03 | 4.97±0.05 |
| E-10 | 0.52 | 2.49±0.03 | 12.2±0.24 |

summarized in Table 2. The weight percent of FeTPP(OH)₄ (7.44 %) was estimated from the iron content (1.33 $\mu\text{mol mg}^{-1}$), and the values were in good agreement with the value calculated from the formula (7.27%). This supports the conclusion that the molar concentrations of FeTPP(OH)₄ and resol catalysts in aqueous solutions can be determined based on the Fe content of the prepared samples. The percent of FeTPP(OH)₄ bound to HA-Me for samples E-6 and E-10 were estimated from their Fe contents in Table 2 and the amount of FeTPP(OH)₄ initially added: 53.4% for E-6; 91.9% for E-10. These results indicate that more FeTPP(OH)₄ was incorporated into HA-Me, when 1,10-dibromodecane was used as the spacer molecule.

Figure 2 shows the SEC chromatograms for HA-Me, E-6 and E-10. The weight average molecular weights for E-6 (23000) and E-10 (30000) were significantly larger than that for HA-Me (2600), indicating the incorporation of FeTPP(OH)₄ into HA. The kinetics of the self-degradation of iron(III)-porphyrin in the presence of KHSO₅ can be evaluated by monitoring the disappearance of the Soret band for porphyrins (Fukushima and Tatsumi, 2006).

Iron(III)-porphyrin catalysts are rapidly inac-

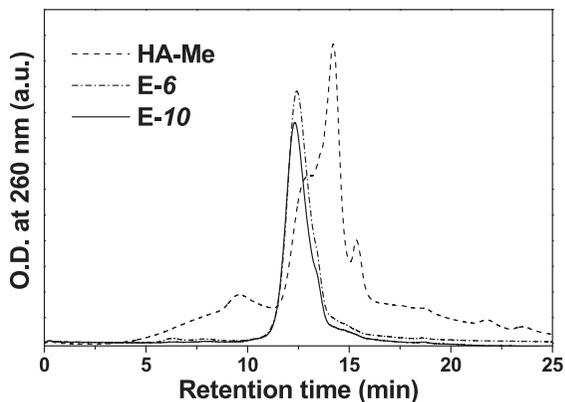


Fig. 2. SEC chromatograms of HA-Me, E-6 and E-10.

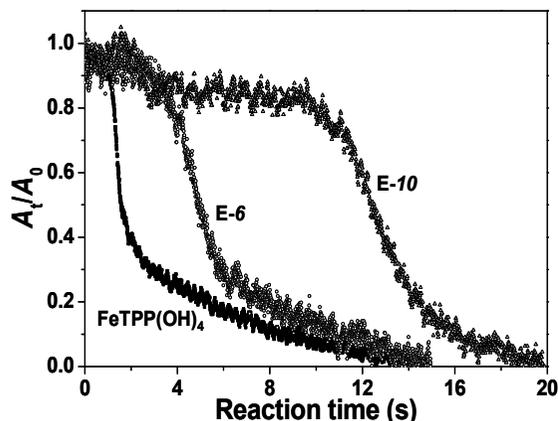


Fig. 3. Self-degradation kinetic curves for FeTPP(OH)_4 and the prepared catalysts at pH 6. [Catalysts] $5 \mu\text{M}$, $[\text{KHSO}_5]$ 1 mM , 25°C .

tivated by self-degradation in the presence of peroxides, such as KHSO_5 . The kinetics of iron(III)-porphyrin self-degradation can be evaluated by monitoring the decolorization of the Soret band (Fukushima and Tatsumi, 2006). Figure 3 shows the kinetic curves for the self-degradation of FeTPP(OH)_4 , E-6 and E-10 ($5 \mu\text{M}$) in the presence of KHSO_5 (1 mM) at pH 6. A_0 and A_t on the y-axis represent the absorbances that correspond to the catalyst concentration before and after the addition of KHSO_5 , respectively. As shown in the kinetic curves in Fig. 3, after an initial period in which the catalysts were gradually degraded, they then underwent rapid degradation. Due to the complicated nature of catalyst degradation reactions, it is not possible to elucidate the nature of the overall reactions. Thus, the half-lives of the catalysts ($t_{1/2}$) were estimated at $A_t/A_0 = 0.5$ in the kinetic curves. The estimated $t_{1/2}$ values at pH 4 and 6 are summarized in Table 2. The $t_{1/2}$ values for E-6 and E-10 were larger than those for FeTPP(OH)_4 at pH 4 and 6, indicating

that catalyst self-degradation was retarded in the catalysts prepared via the production of ether-linkages. In addition, the retardation was more significant for sample E-10 than for sample E-6.

Catalytic activity of prepared catalysts

Figure 4a shows data for the percent PCP degradation at pH 4 and 6. The percentage of PCP degradation for the immobilized catalysts was significantly larger than those for FeTPP(OH)_4 . It should also be noted that the levels of PCP degradation for E-10 were slightly larger than those for E-6. These results are consistent with the results for the retardation of self-degradation (Table 2). Therefore, length of the alkyl-chains of the dibromoalkanes used appear to be an important factor in terms of determining the stability and activity of immobilized catalyst between FeTPP(OH)_4 and HA via ether-linkages.

Figure 4b shows the concentrations of Cl released as a result of the degradation of PCP. The levels of dechlorination for E-6 and E-10 were slightly higher than those for FeTPP(OH)_4 . In addition, the extent of dechlorination for E-10 was higher than that for E-6. The numbers of chlorine atoms, which were calculated by dividing the $[\text{Cl}]$ by the degraded $[\text{PCP}]$, were in the range of 1.4 – 1.7. This suggests that byproducts comprised of tetra- and/or tri-chlorinated

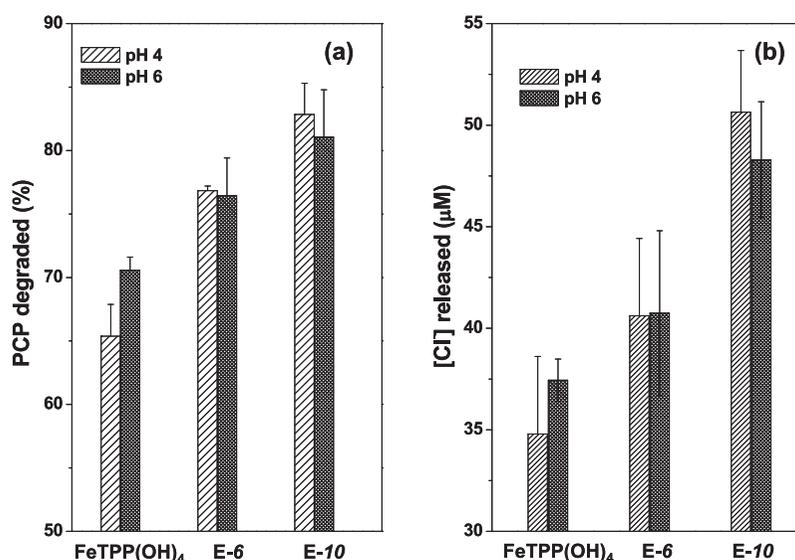


Fig. 4. Percent PCP degradation (a) and $[\text{Cl}]$ released as the result of PCP degradation (b). $[\text{PCP}]_0$ $37.5 \mu\text{M}$, $[\text{KHSO}_5]$ 1 mM , [catalyst] $5 \mu\text{M}$, reaction time 60 min at 25°C .

compounds are produced as the result of PCP oxidation. To identify these byproducts, reaction mixtures at pH 4 were extracted with *n*-hexane and the extracts were analyzed by a GC/MS technique. *Para*- and *ortho*-tetrachloroquinones (TeCQs) and octachlorodibenzo-*p*-dioxin (OCDD) were detected, as reported in previous reports concerning the oxidation of PCP (Fukushima et al., 2003). The percent of PCP conversion to TeCQs were as follows: FeTPP(OH)₄ 20%; E-6 12%; E-10 7.1%. The percentage of PCP conversion to OCDD were as follows: FeTPP(OH)₄ 5.0%; E-6 2.7%; E-10 2.8%. These results show that the levels of TeCQs and OCDD for E-6 and E-10 are smaller than those for FeTPP(OH)₄.

Conclusions

Immobilized catalysts, prepared via the formation of ether-linkages between phenolic hydroxyl groups in FeTPP(OH)₄ and HA, were effective in terms of retarding the self-degradation of catalysts and in enhancing their catalytic activity for PCP degradation, compared to an unmodified catalyst, FeTPP(OH)₄. Although the retardation of self-degradation was greater at pH 6 compared to that at pH 4, the extent of PCP degradation was relatively constant at both pH values. The increase in *t*_{1/2} values for catalyst self-degradation and the levels of PCP oxidation were greater for sample E-10 than for sample E-6. These results suggest that the length of the alkyl-chain in the linkage is an important factor in determining catalyst stability and for enhancing catalytic activity.

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References

- Del Rio, J.C., Hatcher, P.G. (1996) In: *Humic and Fulvic Acids. Isolation, Structure, and Environmental Role*. Gaffney, J.S., Marley, N.A., Clark, S.B. Eds.; American Chemical Society, Washington DC, pp.78-95.
- Fukushima, M., Ichikawa, H., Kawasaki, M., Sawada, A., Morimoto, K., Tatsumi, K. (2003) Effects of humic substances on the pattern of oxidation products of pentachlorophenol induced by a biomimetic catalytic system using tetra(*p*-sulfophenyl)porphineiron(III) and KHSO₅. *Environ. Sci. Technol.* **37**, 386-394.
- Fukushima, M., Shigematsu, S. (2008) Introduction of 5,10,15,20- tetrakis(4-hydroxyphenyl)-porphineiron (III) into humic acid via formaldehyde polycondensation. *J. Mol. Catal. A-Chem.* **293**, 103-109.
- Fukushima, M., Tanabe, Y., Morimoto, K., Tatsumi, K. (2007) Role of humic acid fraction with higher aromaticity in enhancing the activity of a biomimetic catalyst, tetra(*p*-sulfonatophenyl)porphineiron(III). *Biomacromolecules* **8**, 386-391.
- Fukushima, M., Tatsumi, K. (2006) Complex formation of water-soluble iron(III)-porphyrin with humic acids and their effects on the catalytic oxidation of pentachlorophenol. *J. Mol. Catal. A-Chem.* **245**, 178-184.
- Gao, G., Schwardt, O., Ernst, B. (2004) Synthesis of aryl sialosides using Mitsunobu conditions. *Carbohydr. Res.* **339**, 2835-2840.
- Ikeya, K., Ishida, Y., Ohtani, H., Watanabe, A. (2006) Effect of off-line methylation using carbanion and methyl iodide on pyrolysis-gas chromatographic analysis of humic and fulvic acids. *J. Anal. Appl. Pyrol.* **75**, 174-180.
- Shukla, R.S., Robert, A., Meunier B. (1996) Kinetic investigations of oxidative degradation of aromatic pollutant 2,4,6-trichlorophenol by an iron-porphyrin complex, a model of ligninase, *J. Mol. Catal. A-Chem.* **113**, 45-49.
- Smith, J.R.L. (1994) In: *Metalloporphyrins in Catalytic Oxidations*. Sheldon, R.A. Ed.; Dekker, New York, pp.325-368.
- Swift, R.S. (1996) In: *Methods of Soil Analysis Part 3. Chemical Methods*. Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N. Tabatabai, M.A., Johnson, C.T., Summer, M.E. Eds.; Soil Science Society of America, Madison, pp. 1018-1020.
- Tan, K.H. (2003) In: *Humic Matter in Soil and the Environment. Principles and Controversies*. Dekker, New York, pp. 155-162.
- Uno, H., Takata, K., Mizutani, Y. (1991) Polymerization of propylene oxide catalyzed by fixed aluminum porphyrin. *Reactive Polymers* **15**, 121-129.