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Letter

The catalysis of some novel polystyrene-supported porphyrinatomanganese(III) in hydroxylation of cyclohexane with molecular oxygen

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Abstract

Some novel polystyrene-supported porphyrinatomanganese(III) in which alkyl group is bonded to the surface of polystyrene, PS-[Mn(HPTPP)Cl](C_nH_{2n+1}) (n = 2, 6, 8, 18), have been synthesized. Their catalytic activities to hydroxylate cyclohexane in PS-[Mn(HPTPP)Cl](C_nH_{2n+1})–O_2–ascrobate system have been found to be higher compared with corresponding non-supported porphyrinatomanganese(III) and increase with the increase of the length of alkyl. These results are discussed in the point of view of metalloporphyrin microenvironment.

Keywords: Alkylated polystyrene; Polystyrene-supported porphyrinatomanganese(III); Catalysis; Hydroxylation; Cyclohexane

1. Indroduction

As we know, the hydrophobic environment produced by a protein chain folded about the binding site of cytochrome P450 play an important part in the process of the hydroxylation of substrate. The lack of the feature of this hydrophobic environment may be one of the reasons that the model of cytochrome P450 has a limited hydroxylation catalytic capability under mild condition. Great efforts have been made to the chemical modification of metalloporphyrin microenvironment in the studies of cytochrome P450 model. It is found to be effective using organic polymers [1–8], inorganic polymers [9–12], phospholipid bilayer membrane [13], water-soluble polymers (e.g. polypetptide [14]), cyclodextrin [15,16] and one metal-free porphyrin in *p/p* porphyrin dimer linked with flexible alkyl chain as microenvironment of metalloprophyrin [17–19] to increase the catalytic activities of metalloporphyrins. Among the models of metalloporphyrin microenvironment, the derivatives of polystyrene are often utilized, because they can provide suitable microenvironment for the 'accommodation' of porphyrin catalytic centers. On the basis of considering the effect of stereostructure of porphyrinatoiron(III) molecule relative to surface of polystyrene on the catalytic activity of porphyrinatoiron [7,8], in this letter, we report the preparation of some alkylated polystyrene-supported porphyrinatomanganese(III) and their catalysis

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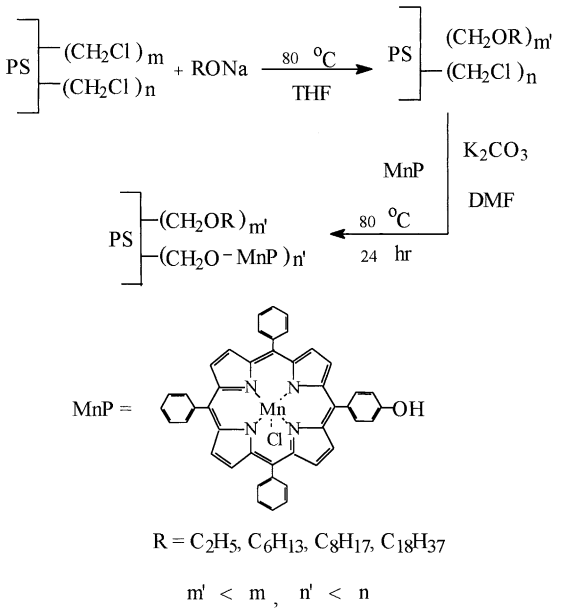

Fig. 1. The strategy to prepare alkylated polystyrene-supported porphyrinatomanganese(III).

in hydroxylation of cyclohexane with molecular oxygen.

2. Synthesis and characterization of alkylated polystyrene-supported porphyrinatomanganese-(III)

The strategy to prepare these novel polystyrene-supported porphyrinatomanganese(III) is to modify the polystyrene by alkyl first and then to bond porphyrinatomanganese(III) to the alkylated polystyrene, which is shown in Fig. 1. The modification of polystyrene was performed by reaction of chloromethylated polystyrene with sodium salt of alcohols. 10.0 g chloromethylated polystyrene (17% Cl, 7% divinyl benzene cross-linked) soaked in THF solution for 24 h beforehand was added to 100 ml THF solution of $C_nH_{2n+1}ONa$ ($n = 2, 6, 8, 18$) which were prepared freshly by the reaction of alcohol and sodium in THF. The mole ratio of sodium salt of alcohol to chlorine in chloromethylated polystyrene is about 1:2. The mixture was refluxed for 24 h with magnetic stirring at 80°C. After cooling, the resins were filtered and washed with acetone, ethanol and water successively until no chloric ion has been examined by $AgNO_3/HNO_3$. The residues were dried in vacuum for 24 h at 80°C, then PS-(CH_2Cl) (C_nH_{2n+1}) ($n = 2, 6, 8, 18$) were obtained. All the filtrate were collected carefully and 1.0 mol/l $AgNO_3/HNO_3$ solution was added to the filtrate concentrated beforehand. Because, we scarcely detect any AgCl by adding $AgNO_3/HNO_3$ in the control experiment in which no $C_nH_{2n+1}ONa$ was added, so the alkyl content can be determined according the weigh of AgCl and the results are: PS-(CH_2Cl) (C_2H_5), 7.92% (1.76×10^{-3} mol/g-C_2H_5); PS-(CH_2Cl) (C_6H_{13}), 9.24% (9.15×10^{-4} mol/g-C_6H_{13}); PS-(CH_2Cl) (C_8H_{17}), 10.22% (7.92×10^{-4} mol/g-C_8H_{17}); PS-(CH_2Cl) ($C_{18}H_{37}$), 9.08% (3.38×10^{-4} mol/g-$C_{18}H_{37}$).

Because, only parts of the chloromethyl on choloromethylated polystyrene had reacted with sodium salt of alcohol, the polystyrene-supported porphyrinatomanganese(III) can be prepared by the reaction of the remained chloromethyl on chloromethylated polystyrene with porphyrinatomanganese(III). The method to bond porphyrinatomanganese(III) to the alkylated polystyrene is similar to the literature we reported before [7,8]. 3.0 g PS-(CH_2Cl) (C_nH_{2n+1}) ($n = 2, 6, 8, 18$) (immersed in DMF for 24 h), 0.5 g anhydrous K_2CO_3 and 150 mg 5-(4-hydroxyl)phenyl-10,15,20-triphenylporphyrinatomanganese(III) chloride were added to 100 ml DMF. The mixture was refluxed for 4 h at 90°C. After cooling, filtering and washing, the residues were extracted with 1,2-dichlomethane in Soxhlet Extracter until no porphyrinatomanganese(III) can be examined in filtrates. The residues were dried in vacuum for 24 h at 60°C and the green products PS-[Mn(HPTPP)Cl](C_nH_{2n+1}) ($n = 2, 6, 8, 18$) were obtained. The porphyrinatomanganese(III) contents in these alkylated polystyrene-supported porphyrinatomanganese(III) determined by analyzing the manganese content using ICP technology are as follow: PS-[Mn(HPTPP)Cl](C_2H_5), 1.74% (2.55×10^{-5} mol/g); PS-[Mn(HPTPP)Cl](C_6H_{13}), 1.50% (2.20×10^{-5} mol/g); PS-[Mn(HPTPP)Cl](C_8H_{17}), 1.20% (1.76×10^{-5} mol/g); PS-[Mn(HPTPP)Cl]($C_{18}H_{37}$), 3.89% (5.70×10^{-5} mol/g).

UV–VIS, IR and EPR spectra of these alkylated polystyrene-supported porphyrinatomanganese(III) were measured and indicated the porphyrinatoman-

ganese(III) are covalently bonded to polystyrene. Solid state UV–VIS spectra showed typical peaks of porphyrinatomangese(III) and the Soret band and Q-band are all red-shifting.[2] EPR data ($\bar{g} = 2.0165$) also indicated the presence of high-spin porphyrinatomanganese(III). Solid state IR spectra showed three new vibration bands of ν(C–O–C) at 1245, 1045 and 558 cm^{-1}, which were resulted from the reaction between the $–CH_2Cl$ group in polystyrene and the –OH group in the phenyl ring of porphyrinatomanganese(III) or the –ONa group in sodium salt of alcohol.

3. Catalysis of alkylated polystyrene-supported porphyrinatomanganese(III) in hydroxylation of cyclohexane with molecular oxygen

The hydroxylation of cyclohexane in PS-[Mn(HPTPP)Cl](C_nH_{2n+1})–O_2–ascrobate system was carried out in a specially constructed reaction vessel at 30.0 ± 0.1°C. The catalytic system consist of the alkylated polystyrene-supported porphyrinatomanganese(III) or non-supported porphyrinatomanganese(III), coreductant (1.0 mmol ascrobate, 4.0×10^{-2} mmol thiosalicylic acid), substrate(cyclohexane 5.55 mmol), actone/water (9:1, 10 ml) and pure oxygen (101 kPa). The products were detected and analyzed by GC (Shimadzu GC-9A) and *n*-pentanol was used as internal standard. The results both in alkylated polystyrene-supported porphyrinatomanganese(III) system and non-supported porphyrinatomanganese(III) system are all listed in Table 1. As it is shown in Table 1, all the alkylated polystyrene-supported porphyrinatomanganese(III) have higher catalytic activities compared with corresponding non-supported porphyrinatomanganese(III), which is consistent with the result of polystyrene-supported porphyrinatoiron(III) we reported before [7,8]. It is worth noting that the length of alkyl bonded to polystyrene have an effect on the total turnovers of alkylated polystyrene-supported porphyrinatomanganese(III) and the order of catalytic activities for them is PS-[Mn(HPTPP)Cl] (C_2H_5) < PS-[Mn(HPTPP)Cl] (C_6H_{13}) < PS-[Mn(HPTPP)Cl] (C_8H_{17}) < PS-[Mn(HPTPP)Cl]($C_{18}H_{37}$). The fact that the catalytic activities of alkylated polystyrene-supported porphyrinatomanganese(III) increase with the increase of the length of alkyl demonstrate unambiguously the microenvironment of porphyrinatomanganese(III) caused by the alkyl chain play an important part in the catalysis process. Considering the length of corresponding alkyl chain and the distance between a phenyl and the center of porphyrin ring in porphyrinatomanganese(III) may be of advantage to find out the role of alkyl chain in the catalysis of porphyrinatomanganese(III). The lengths of alkyl chains calculated from the data of C–C band are: $–C_2H_5$, 127 pm; $–C_6H_{13}$, 634 pm; $–C_8H_{17}$, 889 pm; $–C_{18}H_{37}$ 2157 pm. The distance between a phenyl and the center of porphyrin ring in porphyrinatomanganese(III) obtained from the crystal and molecular structure of Fe(TPP)Cl determined by single-crystal diffraction technique [20] is ca. 960 pm. These data are diagramed in Fig. 2. We believed that the alkyl group bonded on the surface of the polystyrene will bind together in part area by the hydrophobia, especial in our system the solvent is a mixture of acetone and water. Because, the length of octadecyl ($–C_{18}H_{37}$) is longer than the size of porphyrin ring, it is possible that the porphyrinatomanganese(III) is wrapped up by these octadecyl and the hydrophobic

Table 1
The catalytic activities of alkylated polystyrene-supported porphyrinatomangnese(III) and non-supported porphyrinatomanganese(III)

Catalysts[a]	Product amount[b]/10^{-4} mol (turnover number[c])		
	Cyclohexanol	Cyclohexanone	Total
1	2.13 (44.19)	1.19 (24.67)	3.32 (68.86)
2	2.10 (48.74)	1.05 (24.49)	3.15 (73.23)
3	2.04 (53.77)	1.00 (26.26)	3.04 (80.03)
4	5.58 (130.68)	1.03 (24.19)	6.61 (154.87)
5	1.93 (20.24)	0.97 (10.20)	2.90 (30.45)

[a] (1): PS-[Mn(III)(HPTPP)Cl](C_2H_5), 4.82×10^{-3} mmol; (2): PS-[Mn(III)(HPTPP)Cl](C_6H_{13}), 4.30×10^{-3} mmol; (3): PS-[Mn(III)(HPTPP)Cl](C_8H_{17}), 3.80×10^{-3} mmol; (4): PS-[Mn(HPTPP)Cl]($C_{18}H_{37}$), 4.27×10^{-3} mmol; (5): [Mn(III)(HPTPP)Cl], 9.52×10^{-3} mmol.
[b] Reaction time, 0.5 h.
[c] Turnover number = product (mol)/catalyst (mol).

[2] For example, the bands of PS-[Mn(HPTPP)Cl]($C_{18}H_{37}$) are 451.4, 518.0, 566.4 and 609.4 nm, the bands of the mixture of PS-($C_{18}H_{37}$) and [Mn(HPTPP)Cl] are 445.8, 507.0, 588.8 and 592.4 nm.

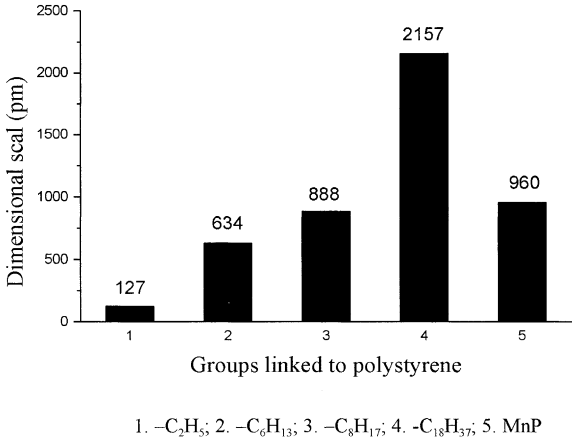

Fig. 2. The diagram of the length of the various alkyls and the distance between a phenyl and the center of porphyrin ring in porphyrinatomanganese(III).

microenvironment of porphyrinatomanganese(III) resulted from the twist and fold of the long alkyl chains may be similar to that of the active center of natural cytochrome P450. As we know, the key steps [21] in the catalytic cycle that cytochrome P450 catalyze hydroxylation of substrates with molecular oxygen, such as reduction of the high spin ferric complex to ferrous complex, the binding of dioxygen to the ferrous complex, the formation of the highly active [Fe(V)=O] species and the oxygen transfer from [Fe(V)=O] species to substrate are all related to the hydrophobic microenvironment — the hydrophobic cavity formed in three-dimensional structure of the protein part. According to this point of view, it is not difficult to explain PS-[Mn(HPTPP)Cl]($C_{18}H_{37}$) has the highest catalytic activity in our system. For PS-[Mn(HPTPP)Cl](C_2H_5), it is difficult to form such hydrophobic microenvironment, so its catalytic activity is relatively low. With the increase of the length of alkyl chain, porphyrinatomanganese(III) in PS-[Mn(HPTPP)Cl](C_nH_{2n+1}) may be wraped up more or less by the alkyl. These may be the reason that the catalytic activity of PS-[Mn(HPTPP)Cl](C_8H_{17}) slight increase comparing with that of PS-[Mn(HPTPP)Cl](C_6H_{13}) and PS-[Mn(HPTPP)Cl](C_2H_5). The preliminary studies on the reuse of the alkylated polystyrene-supported porphyrinatomanganese(III) indicate the resins can be reused to catalyze hydroxylation of cyclohexane and reused resins retain high catalytic activity. For example, turnover number of PS-[Mn(HPTPP)Cl](C_8H_{17}) in the first reuse is 71.11.

4. Conclusion

By using the method that polystyrene is modified by alkyl first and then porphyrinatomanganese(III) is bonded to the alkyiated polystyrene, some novel polystyrene-supported porphyrinatomanganese(III) in which alkyl is bonded on the surface of polystyrene and act as the microenvironment of porphyrinatomanganese(III) are synthesized. Their catalytic activities to hydroxylate cyclohexane in PS-[Mn(HPTPP)Cl](C_nH_{2n+1})–O_2–ascrobate system have been found to be higher compared with corresponding non-supported porphyrinatomanganese(III), which may be attributable to the hydrophobic microenvironment of porphyrinatomanganese(III) caused by the binding state of alkyl groups. It seems binding long alkyl to resins is a good method to model the microenvironment of the active center of cytochrome P450.

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References

[1] T. Mathew, S. Kuriakose, J. Porphyrins and Phthalocyanines 3 (1999) 316.
[2] T. Mathew, S. Kuriakose, J. Appl. Polymer Sci. 69 (1998) 89.
[3] P. Anzenbacher, V. Král, K. Jursiková, J. Günterová, A. Kasal, J. Mol. Catal. A: Chem. 118 (1997) 63.
[4] P. Anzenbacher, V. Král, J. Mol. Catal. A: Chem. 97 (1995) 2123.
[5] H. Uno, K. Takata, Y. Mizutani, React. Polym. 92 (1991) 297.
[6] K. Marugama, H. Tamiaki, S. Kawabata, J. Chem. Soc., Perkin Trans. 2 (1986) 543.
[7] Z.-L. Liu, J.-W. Huang, L.-N. Ji, J. Mol. Catal. A: Chem. 104 (1996) L193.
[8] W.-J. Mei, J.-W. Huang, S.-G. Hu, L.-N. Ji, Acta Scienliarnum Naturalium Universitatic Sun Yatseni 39 (1) (2000) 125.

[9] P.E.F. Neys, A. Severeyns, I.F.J. Vankelecom, J. Mol. Catal. A: Chem. 144 (1999) 373.
[10] P.E.F. Neys, I.F.J. Vankelecom, R.F. Parton, J. Mol. Catal. A: Chem. 126 (1997) L9.
[11] H.S. Hilal, C. Kim, A.F. Schreiner, J. Mol. Catal. 81 (1993) 157.
[12] H.S. Hilal, W. Jondi, S.K. Khalafl, A. Keilani, M. Saleiman, A.F. Schreiner, J. Catal.: Chem. 56 (1996) 1253.
[13] K. Ilda, M. Nango, K. Okada, S. Matsumoto, M. Matsuura, K. Yamashita, K. Tsuda, Y. Kurono, Y. Kimura, Chem. Lett. (1994) 1307.
[14] T. Mori, T.Santa and M. Hirobe, Tetrahedron Lett. 26 (1985) 553.
[15] Y. Kuroda, T. Hiroshige, T. Sera, Y. Shiroiwa, H. Takana, H. Ogoshi, J. Am. Chem. Soc. 111 (1989) 1912.
[16] Y. Kuroda, T. Hiroshige, T. Sera, H. Ogoshi, Carbohyr. Res. 192 (1989) 347.
[17] J.-W. Huang, Z.-L. Liu, X.-R. Gao, D. Yang, X.-Y. Peng, L.-N. Ji, J. Mol. Catal. A: Chem. 111 (1996) 261.
[18] Q.-Z. Ren, J.-W. Huang, X.-B. Peng, L.-N. Ji, J. Mol. Catal. A: Chem. 148 (1999) 9.
[19] Q.-Z. Ren, J.-W. Huang, Z.-L. Liu, L.-N. Ji, S. Afr. J. Chem. 50 (1997) 181.
[20] J.L. Hoard, G.H. Cohen, M.D. Glick, J. Am. Chem. Soc. 89 (1967) 1992.
[21] D. Mansuy, Pure Appl. Chem. 59 (1987) 759.