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PREPARATION AND CATALYTIC PROPERTIES OF POLYMER-BOUND SCHIFF BASE TERNARY COMPLEXES

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ABSTRACT

The polymer-bound Schiff base ternary cobalt complexes (PS-SalPhe-Co-L (L = Phen, Bipy and 8HQ)) have been prepared from the polymer bound Schiff base ligand, cobalt salt and the second ligand, such as 1,10-phenanthroline(phen), 2,2'-bipyridyl(bipy) and 8-quinolinol(8HQ). The polymer-bound Schiff base ternary cobalt complexes were characterized by the infrared spectra and ICP-AES. The catalytic activity of the complexes has been studied in aerobic epoxidation of long-chain linear aliphatic olefins. It showed that 1-octene or 1-decene can be directly oxidized by molecular oxygen catalyzed by PS-SalPhe-Co-L (L = Phen, Bipy and 8HQ), which afford the 1,2-epoxy alkane.

Key Words: Aerobic oxidation; Polymer-bound Schiff base ternary complexes; Linear aliphatic olefins; Epoxidation

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INTRODUCTION

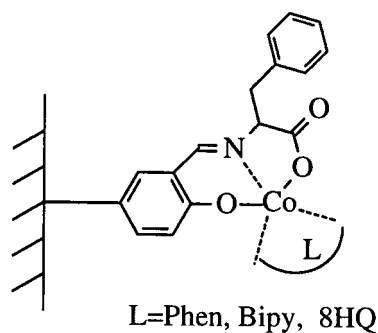
The finding of efficient catalysts for the selective insertion of one oxygen atom from oxygen donors, like dioxygen, hydrogen peroxide, alkylhydroperoxide, sodium hypochlorite or iodosobenzene into various organic molecules, under mild conditions, remains a difficult challenge in the fields of chemical and biological catalysis.^[1] Synthetic metal complexes, such as metalloporphyrins,^[2-4] phthalocyanines, metal-Salen^[5-7] for catalytic oxidation of hydrocarbons, mimicking the action of cytochrome P-450 based enzymes has been studied extensively.^[8,9] It was also found that the stability of the metal complexes catalyst may be improved by polymerization of complexes or being bonded on polymer.^[10-12]

For the potentially practical use of the catalytic systems in oxidation, the research emphasis has been directed to the use of cheap, easily accessible and environmentally friendly oxidants such as molecular oxygen or hydrogen peroxide. The Schiff-based complexes are relatively easy to be prepared than that of metallic-porphyrin complexes.^[13] In this paper, the effect of the small molecular ligand in aerobic epoxidation of long-chain linear aliphatic olefins has been studied, which showed that olefins could be effectively oxidized by molecular oxygen catalyzed by polymer-bound Schiff base ternary cobalt complexes.

EXPERIMENTAL

Materials and Equipment

Both phenylalanine and 2,4-dihydroxybenzaldehyde were obtained from Aldrich Company and used without further purification. Olefins were purified by distillation just before use. Other reagents, such as 1,10-phenanthroline(phen), 2,2'-bipyridyl(bipy), 8-quinolinol(8HQ), ethanol and metals salts were used as received.



Scheme 1. PS-SalPhe-Co-L.

IR spectra were recorded in KBr disks with an Alpha-centauri FT-IR spectrophotometer. The metal contents were detected on a model ARL-3520 Inductively Coupled Plasmas Atomic Emission Spectrometry of USA. The reaction products of oxidation were determined and analyzed by using a Shimadzu GC-16A gas chromatograph, QP-1000A GC/MS system, a GC-IR system(HP 5890 II GC, and a Bio-Rad 65A FTS IR system).

Synthesis of Polymer Bound Schiff Base (PS-SalPhe)

The polymer bound salicylaldehyde (PS-Sal) and the polymer bound salicylaldehyde amine acid Schiff base ligand (PS-SalPhe) were synthesized according to the literature method.^[13]

Synthesis of Polymer Bound Schiff Base Ternary Complexes

0.7 g of PS-SalPhe was added into 30 mL of ethanol, the mixture was stirred for 1 h. After adding 2.0 g of 1,10-phenanthroline, 2.5 g of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, the reaction mixture was stirred in 50-60°C for 24 h. Cooling to room temperature, the product of the polymer ternary complex was filtrated, then washed with water and alcohol separately until there was no color in the filtrate. After dried under vacuum, the polymer bound Schiff base-cobalt-phenanthroline ternary complex (PS-SalPhe-Co-Phen) was obtained.

Other polymer bound Schiff base ternary complexes (PS-SalPhe-Co-L), such as the polymer bound Schiff base-cobalt-bipyridyl ternary complex (PS-SalPhe-Co-Bipy), the polymer bound Schiff base-cobalt-quinolinol ternary complex (PS-SalPhe-Co-8HQ), were obtained by above method.

Oxidation Procedure

Typical oxidation procedure: A glass flask was charged with PS-SalPhe-Co-L (5 mg) and substrate (1 mL). The dry oxygen was filled from the gauge glass and the atmosphere was discharged out of the glass reactor with the gas outlet tube. After closing the gas outlet tube, the reactor was put into a heating bath, the temperature of which was kept at 100°C, and stirring was started. The consumption of oxygen was measured and calculated by gauge glass. After reacting for 10 h, the reaction products were analyzed by using a Shimadzu GC-16A gas chromatograph with a 5 m × 3 mm OV-17 column, a Shimadzu QP-1000A GC/MS system, and a GC-IR system(HP 5890 II GC and Bio-Rad 65A FTS IR system, Interface: GC/C 32 GC-IR; Column: SE54 (25 m × 0.32 mm); FID; Inj. 260°C, Dect.260°C; Init. Temp.100°C, Init Time: 3 min, Rate 10°C/min, Final Temp. 220°C, Flow: 1.41 mL/min).

Characterization of the Polymer Bound Schiff-Based Ligand and Its Ternary Complexes

As shown in Table 1, IR spectra showed that asymmetric stretching vibration absorption band (ν_{as}) of COO^- appear at 1599 cm^{-1} , $\nu_{s\text{COO}^-}$ at 1422 cm^{-1} , $\nu_{\text{C}=\text{N}}$ at 1678 cm^{-1} , and $\nu_{\text{Ph-O}}$ near 1260 cm^{-1} for polymer bound Schiff base ternary complexes, which were different from PS-SalPhe. As the macrocycle backbones are influenced by metal ion, the M-N bond and M-O bond of the complexes appear near 548 cm^{-1} and 461 cm^{-1} , respectively. A wide peak appears near 3400 cm^{-1} , which belong to water. Table 2 shows the result of ICP-AES.

The structure of ligand (PS-SalPhe) and the coordination of the complex PS-SalPhe-Co were confirmed by the small area X-ray photoelectron spectroscopy.^[13]

RESULTS AND DISCUSSION

Aerobic Epoxidation of 1-Octene

The linear aliphatic olefins 1,1-octene, can be directly oxidized by molecular oxygen in the presence of the polymer bound Schiff base ternary complexes without any reductants or solvents, which affords the 1,2-epoxy alkane 2.

Table 1. IR Data of Polymer Bound Schiff Base Ternary Complexes (cm^{-1})

Complex	$\nu(\text{OH})$	$\nu_{\text{C}=\text{N}}$	$\nu_{\text{COO}(\text{as})}$	$\text{COO}(\text{s})$	$\nu_{\text{C-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$
PS-SalPhe-Co-Bipy	3371	1678	1598	1422	1256	548	461
PS-SalPhe-Co-Phen	3455	1678	1599	1423	1286	549	461
PS-SalPhe-Co-8HQ	3440	1677	1592	1422	1263	553	468

Table 2. The Metal Content in the Polymer Bound Schiff Base Ternary Complexes

Complexes	Metal Content (mol/g)
PS-SalPheCo	8.5×10^{-5}
PS-SalPhe-Co-Bipy	5.8×10^{-5}
PS-SalPhe-Co-Phen	7.6×10^{-5}
PS-SalPhe-Co-8HQ	9.8×10^{-4}

Table 3. The Polymer Bound Schiff Base Ternary Complexes Catalyzed Aerobic Epoxidation of 1-Octene

Catalyst (mg)	Conversion (%)	TON (mol/molCo)	Select (%)
PS-SalPheCo ^a	15.5	5.8×10^3	53.8
PS-SalPhe-Co-Bipy ^b	37.8	8.3×10^3	68.3
PS-SalPhe-Co-Phen ^b	23.8	4.0×10^3	99.0
PS-SalPhe-Co-8HQ ^b	10.1	1.3×10^2	53.5
SalPheCo ^c	60.5	1.2×10^2	50.3
SalPhebipyCo ^c	47.2	1.5×10^3	54.0

Condition: 1-C₈H₁₆:1.00 mL; Catalyst: ^a(2mg), ^b(5mg), ^c(1mg); React.Temp.: 100°C; 10 h.

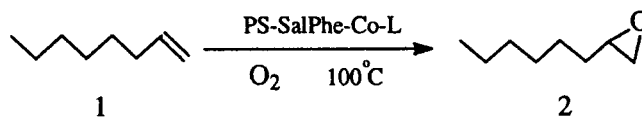


Table 3 shows the results of aerobic epoxidation catalyzed by the polymer bound Schiff base ternary complexes. In general, the selectivity of 1,2-epoxy alkane was from 99% to 50%. It shows that effect of the second ligand is different. Phen and bipy increase as the conversion of linear aliphatic olefins and selectivity is increased. Comparing with small molecular binary and ternary complexes, the polymer bound Schiff base ternary complexes show a higher turnover number.

The influence of the reaction temperature has been studied. Figure 1 illustrates the variation of the conversion of substrate with a different

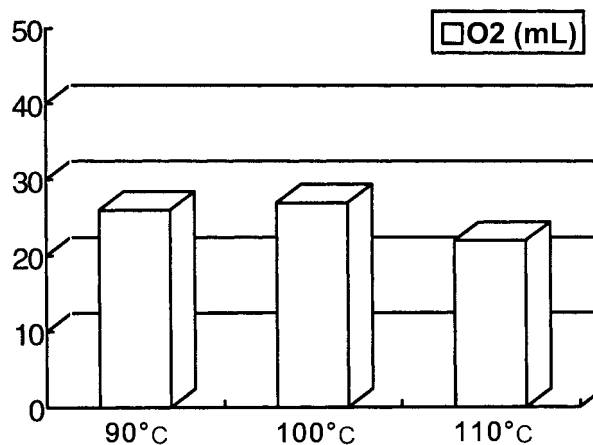


Figure 1. Effect of temperature in catalytic oxidation of the 1-octene catalyzed by PS-SalPhe-Co-Bipy. Substrate: 1 mL; Cat:5 mg, Time: 10 h.

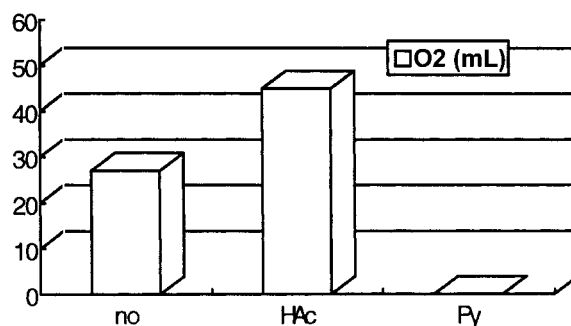


Figure 2. Influence of acid or base in oxidation of 1-octane catalyzed by PS-SalPhe-Co-Bipy. Cat:5 mg, sub:1 mL, Additives: 0.05 mL; 100°C.

reaction temperature in the epoxidation of 1-octene. The oxidation reaction did not happen when the temperature was lower than 80°C. In most of the common solvents, such as alcohol, acetonitrile, methylene dichloride, and cyclohexane, the epoxidation did not happen since their boiling temperature is not higher than 80°C.

It is found that additives influenced activity of the catalyst (Fig. 2). Adding a small amount of acid, such as HOAc, the oxidation reaction would be fast, but pyridine inhibited the reaction. It is suggested that pyridine acts as axial ligand in the polymer complexes.

Figure 3 shows the reusability of the catalyst on catalytic epoxidation. It shows that the catalytic activity of PS-SalPhe-Co-Bipy remained until the fourth circle. The small molecular catalyst, SalGlu-Co and SalPhe-Co-Bipy, could not be reused because they were difficult to be separated.

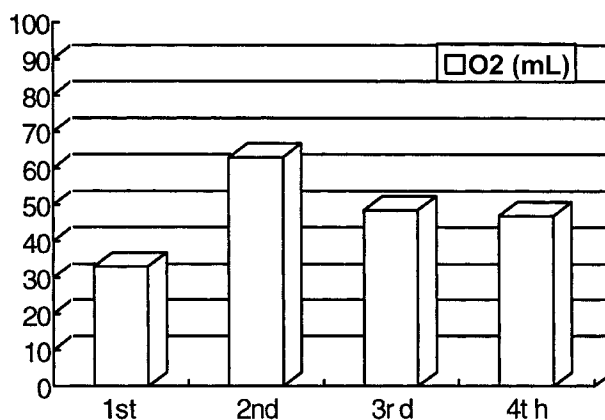


Figure 3. Reusability of PS-SalPhe-Co-Bipy on catalytic epoxidation of 1-octane Cat:5 mg, sub:1 mL, 100°C, 10 h.

Table 4. The Polymer Bound Schiff Base Ternary Complexes Catalyzed Aerobic Epoxidation of 1-Decene

Catalyst (mg)	Conversion (%)	TON (mol/mol Co)	Select (%)
PS-SalPheCo ^a	14.7	1.8×10^3	71.0
PS-SalPhe-Co-Bipy ^a	76.5	1.4×10^4	60.1
PS-SalPhe-Co-Phen ^b	52.9	1.8×10^4	73.5
PS-SalPhe-Co-8HQ ^a	47.1	5.1×10^2	58.1

Condition: 1-C₁₀H₂₀:1.00 mL; Cat: ^a(5 mg), ^b(2 mg); React.Temp.: 100°C; 10 h.

Aerobic Epoxidation of 1-Decene

1-decene can also be directly oxidized by molecular oxygen in the presence of the polymer bound Schiff base ternary complexes without any reductants or solvents, which affords the 1,2-epoxy alkane. Table 4 shows that catalytic activity of the polymer bound Schiff base ternary complexes are higher than that of PS-SalPheCo.

CONCLUSION

The polymer bound Schiff base ternary complex is the available catalyst for epoxidation of linear aliphatic olefins by O₂ without reductant. This kind of catalyst is a potentially important catalyst in chain linear aliphatic olefins oxidation or similar oxidation processes of hydrocarbons. They are environmentally more attractive than oxidation based on stoichiometric amounts of H₂O₂, NaIO₄, Pb(OAc)₄, RuO₄, NaClO or KMnO₄.

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