

Polymeric Salphen-Phthalocyanine Dinuclear Metal Complexes for Activation of Molecular Oxygen

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ABSTRACT: The polymeric Salphen Schiff base-phthalocyanine Co-Cu dinuclear metal complex (PSalphenCo-PcCu) was designed and synthesized through interfacial condensation polymerization. The new sheet polymeric dinuclear metal complex has been characterized by IR spectra, UV-visible spectra, scanning electron microscopy with energy dispersive X-ray analysis and thermogravimetry analysis. Its catalytic activity for activation of molecular oxygen was investigated by using cumene as substrate

without any additive in mild condition. The aerobic oxidation of cumene catalyzed by PSalphenCo-PcCu proved to be a simple and efficient method for obtaining cumene hydroperoxide in a high selectivity. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1999–2005, 2009

Key words: polymeric dinuclear metal complex; polyphthalocyanines; salphen schiff base metal complexes; sheet polymer; molecular oxygen; catalytic oxidation

INTRODUCTION

During the past decades, polymer porphyrin and quasi-porphyrin metal complexes have been attracted much attention for their unusual properties,¹ such as photosensitivity,² photoconductivity,^{3,4} semiconductivity,^{5,6} catalysis,^{7–9} and high thermostability.¹⁰ The phthalocyanines, Salen Schiff-base ligands (Salen = bis(salicylidene)ethylenediamine, and Salphen = bis(salicylidene)-*o*-phenylenediamine) are typical quasi-porphyrin ligands as their structure centers are similar to those of porphyrin. According to the mode of polymerization, polymer phthalocyanine metal complexes include polymer bound phthalocyanines, sheet-like polymeric phthalocyanines, and bridged polymeric phthalocyanines formed by polymerization of square-planar phthalocyanine rings to linear chains.¹¹ Their properties are also different with polymerization mode. The Salen (or Salphen) metal complexes have also been extensively studied as they possess interesting properties related to catalysis and electrochemistry, especially in enantioselectivity. The Salen ligand or metal complexes can also be polymer-

ized by supporting with covalent bond,¹² polymerization,^{13,14} or being encapsulated in surface or cave of supporter.^{15,16} It was found that Schiff base complexes were easily prepared, and polymer chain could increase its stability. However, very few reports about copolymer dimetal complexes of Salen with other kinds of macrocyclic metal complexes. We found that crown ether can be copolymerized with Salen metal complexes, which afforded new kind of heterodinuclear polymer complexes. They were applied in catalytic aerobic oxidation of hydrocarbons.^{17,18} In this paper, the phthalocyanine copper complex [PcCu] has been cocondensation polymerized with Salphen metal complex [SalphenCo], which afforded a new kind of polymeric quasi-porphyrins Co-Cu dinuclear metal complexes (Scheme 1).

EXPERIMENTAL

Materials and equipments

2,4-Dihydroxybenzaldehyde was obtained from Aldrich chemical. Cumene and 1,2-dichloroethane was purified by fractionating distillation just before use. Other reagents and metals salts were commercially available and used as received unless noted otherwise.

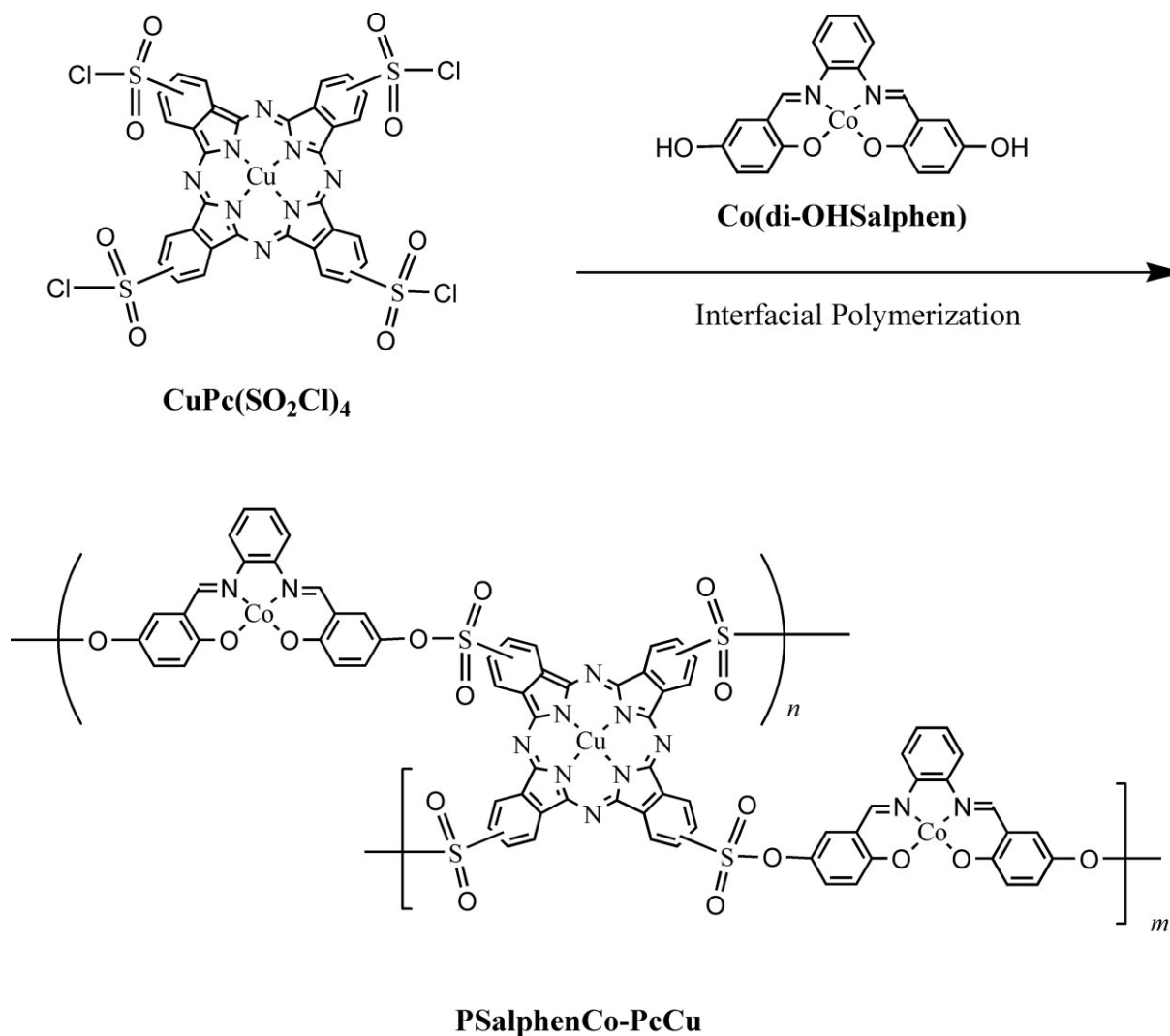
The infrared spectra (IR) were recorded in KBr disks with an α -centauri FT-IR spectrophotometer. Thermogravimetry (TG) analysis was performed on a Shimadzu DT-40 Thermal Analyzer at a heating rate of 10°C/min under argon flow. The UV-Vis spectra were recorded in diffuse reflectance (DRUV-VIS) mode with UV-2500 spectrophotometer of Shimadzu

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Scheme 1 The route for preparation of the polymeric quasi-porphyrins Co-Cu dinuclear metal complex (PSalphenCo-PcCu) with the phthalocyanine copper complex [PcCu] and the Salphen cobalt complex [SalphenCo].

using BaSO₄ as a blank. Scanning electron microscopy (SEM) analysis was performed with a JEOL, JSM 5800 instrument, and an energy dispersive X-ray (EDX) machine (Oxford, Link, ISIS 300) was attached to the instrument to obtain the metal quantification.

Synthesis of the Salphen Schiff-base cobalt complex [Co(diOHSalphen)]

The Co(diOHSalphen) was synthesized by a method based on that described previously.¹⁹ Briefly, using Co²⁺ as template, 2,4-dihydroxybenzaldehyde and *o*-phenylene-diamine (2 : 1/mol : mol) were condensation reacted in propanol under nitrogen protection at 70°C for 8 h with a yield of 80%.

Synthesis of the tetrachlorosulfonylphthalocyanine copper complex [CuPc(SO₂Cl)₄]

The tetrachlorosulfonylphthalocyanine copper complex [CuPc(SO₂Cl)₄] was prepared by a method

described in the literature.²⁰ The reagent of HSO₃Cl (12 g, 0.1 mol) was added dropwise to the dichloromethane solution of PcCu (1 g, 1.74 mmol) with being cooled in an ice-bath under nitrogen. Then, the reaction mixture was refluxed for 4 h at 135–145°C, and then poured into ice. After filtration, the precipitate was washed with 0.1 mol/L of HCl. The products, CuPc(SO₂Cl)₄, were evaporated in vacuum to dryness and provided dark blue powder, yield of 71%.

Preparation of polymeric Salphen-phthalocyanine dinuclear metal complexes (PSalphenCo-PcCu)

The PSalphenCo-PcCu was prepared by interfacial condensation polymerization with [CuPc(SO₂Cl)₄] and Co(diOHSalphen). First, Co(diOHSalphen) (0.81 g, 0.002 mol) was dissolved in 5 mL solution of NaOH (0.8 mol/L) by stirring, and the phase-transfer catalyst (5%) was added, and then stirred for 15 min. To the solution, 2 mL of the solution of

tetrachlorosulfonylphthalocyanine copper [CuPc(SO₂Cl)₄] (0.97 g, 0.001 mol) in 1,2-dichloroethane was added dropwise with vigorously stirring. After stirring for 2 h, the product was isolated by filtration, and washed separately with 10% NaOH solution, ethanol, and H₂O for several times. The polymer complex was obtained with a yield of 60% after being dried under vacuum.

Typical procedure for catalytic aerobic oxidation

The oxidation of organic substrate by atmospheric pressure of molecular oxygen was carried out using a straightforward apparatus. In a typical oxidation reaction, 2 mL of substrate and given amount of catalyst (PSalphenCo-PcCu) were added to a glass reactor (10 mL). The reactor was filled with molecular oxygen using the gauge glass, and the atmosphere was discharged out of the glass reactor with the gas outlet tube. The mixture was heated to a constant temperature in an oil bath and stirred with a magnetic stirring bar. The consumption of oxygen was measured and calculated by the gauge glass. At the end of the reaction time, liquid samples were removed from the reactor vessel and analyzed by using Shimadzu QP-1000A GC/MS system, GL-16A gas chromatograph with a 5 m × 3 mm OV-17 column, 80–200°C (10°C/min), Inj. 220°C, Dect. 220°C.

RESULTS AND DISCUSSION

Characterization

Polymeric Salphen-phthalocyanine dinuclear metal complexes (PSalphenCo-PcCu) and its materials (monomer, small ligands) have been characterized by IR spectra, UV-visible spectra, scanning electron microscopy with energy dispersive X-ray analysis, and thermogravimetry analysis.

The IR spectra

The IR spectra of the polymeric Salphen-phthalocyanine dinuclear metal complex (PSalphenCo-PcCu) and its materials (CuPc, CuPc(SO₂Cl)₄) are shown in Figure 1. The phthalocyanine skeletal vibrations absorption of polymeric metal complex and its materials appeared in 1502–759 cm⁻¹ region.²¹ Compared with the stretch vibration absorption peak of S=O double bond of –SO₂–OH at 1340 cm⁻¹, the vibration absorption peak of –SO₂–Cl shifts to 1375 cm⁻¹. For polymeric dinuclear complex (PSalphenCo-PcCu), the vibration absorption peaks of –SO₂–O– ester bond shift to 1365 cm⁻¹, which verifies that the polymer chain (–CuPc–SO₂–O–SalphenCo–) was obtained. The stretch vibration absorption of C=N bond (ν_{C=N}) of Salphen Schiff

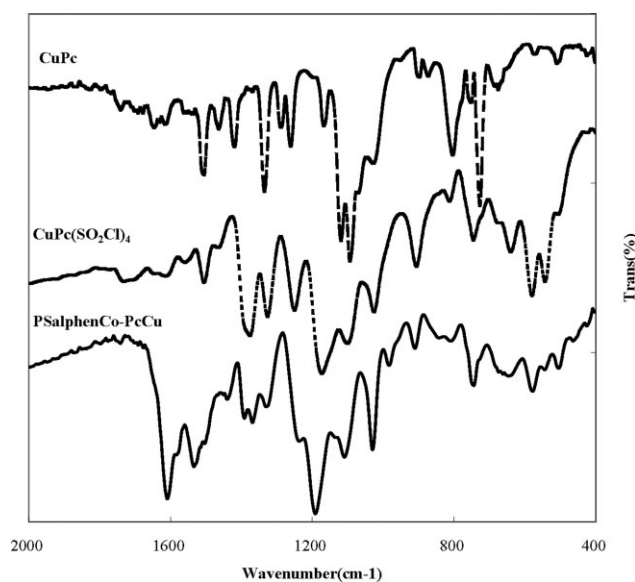


Figure 1 IR spectra of the polymeric Salphen-phthalocyanine dinuclear metal complex (PSalphenCo-PcCu) and its materials (CuPc, CuPc(SO₂Cl)₄) in 2000–400 cm⁻¹ region.

base has also appeared at 1608 cm⁻¹ in PSalphenCo-PcCu. It also showed a new absorption band at 437 cm⁻¹, which assigned to ν(Co–O) absorption of Salphen Schiff base cobalt complex.¹²

UV-Vis spectra

The UV-Vis absorption spectra of the polymeric Salphen-phthalocyanine dinuclear metal complex (PSalphenCo-PcCu) and its materials was obtained in solid state, as most of phthalocyanine metal complexes are insoluble in popular solvents, such as DMF, DMSO, THF, and CHCl₃. The spectra for the solid complexes were recorded in diffuse reflectance (DRUV-VIS) mode using BaSO₄ as a blank. The results are shown in Figure 2. It showed typical electronic spectra with two strong absorption regions, one in the UV region at near 310 nm (B-band) and the other visible region in 550–750 nm (Q-bands).²² Compared with monomer (CuPc), Q-bands were red shifted and showed differences in the absorption coefficients.

The surface images of PSalphenCo-PcCu by SEM

Features of morphology image were investigated by SEM. Figure 3 reveals the surface images of small ligands, Co(diOHSalphen) and CuPc, and the polymeric metal complex (PSalphenCo-PcCu). It was found that the PSalphenCo-PcCu is caky solid whereas two kinds of ligands are all virgulate crystal. The elemental composition of PSalphenCo-PcCu was measured by SEM along with EDX. The

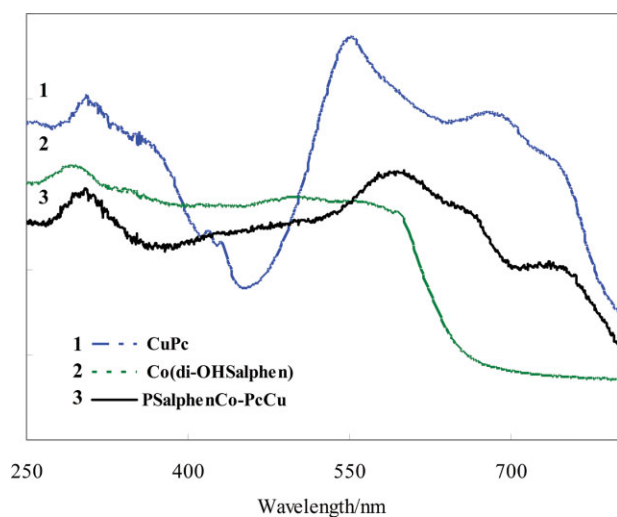


Figure 2 DRUV-VIS spectra of the polymeric Salphenphthalocyanine dinuclear metal complex (PSalphenCo-PcCu) and its materials. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

molecular ratio of Co/Cu was 2.2/1, which is similar to calculated value.

The thermal stability of the polymeric Co-Cu dinuclear metal complex was also measured by TG analysis. One monomer, Co(diOHSalphen), was decomposed at 365–660°C, whose lost weight was about 80%. Another monomer, CuPc, was decomposed at 405–505°C, whose lost weight was also 80%. However, the polymeric Co-Cu dinuclear metal complex was decomposed slowly. About 20% of its weight was lost at 100–500°C, and other 40% of weight was lost in the region of 500–800°C. It indicated that the PSalphenCo-PcCu was more stable than that of monomers. The reason is that the phenol hydroxyl group was converted to ester group after polymerization, which is more stable.

On the basis of above results, it is suggested that the polymeric Co-Cu dinuclear metal complex (PSalphenCo-PcCu) was obtained. As rigid quadri-functional monomer [CuPc(SO₂Cl)₄] and bifunctional

monomer [Co(diOHSalphen)] had condensation polymerized as Scheme 1. We consider that the structure of PSalphenCo-PcCu is a kind of sheet polymer. As the flexibility of such rigid sheet polymer was very low, they could aggregate layer-by-layer, which is shown in Scheme 2. Therefore, the features of morphology image were caky solid. In other side, there should have holes in each polymeric layer. Being simulated by the molecular model, the hole's diameters in such polymer layer should be more than 3 nm. Therefore, the small molecule can easily permeate through such polymer layer. It is available to increase their catalytic activity.

Aerobic oxidation of cumene catalyzed by the polymeric dinuclear metal complex

To investigate catalytic activity for activation of molecular oxygen by PSalphenCo-PcCu, it was devoted to the selective catalytic oxidation of cumene with molecular oxygen. It was found that oxidation preferentially happened in the benzyl carbon of the cumene, which afforded cumene hydroperoxide (CHP) and 2-phenyl-2-propanol (PP)²³ (Scheme 3). Catalytic activity and selectivity of monomers, Co(diOHSalphen) and CuPc, were also investigated at same condition (Table I). In the presence of PSalphenCo-PcCu, the conversion of cumene is to 76%, which is higher than that of monomers. In addition, CHP selectivity (89%) and total selectivity (98%) of products are also high. It means that the polymeric dinuclear metal complex catalyst has high catalytic oxidation activity and selectivity to cumene. We considered that the higher catalytic activity of the PSalphenCo-PcCu is attributed to the following factors: First, after fixing the metal complex into polymer skeleton, the μ -oxo dimer could not be formed. It also prevents the catalytic active center of one unit attack another peripheral group, which prevents to be decomposed by each other.^{24–26} Second, although the average size of polymeric catalyst (about 70 μ m)

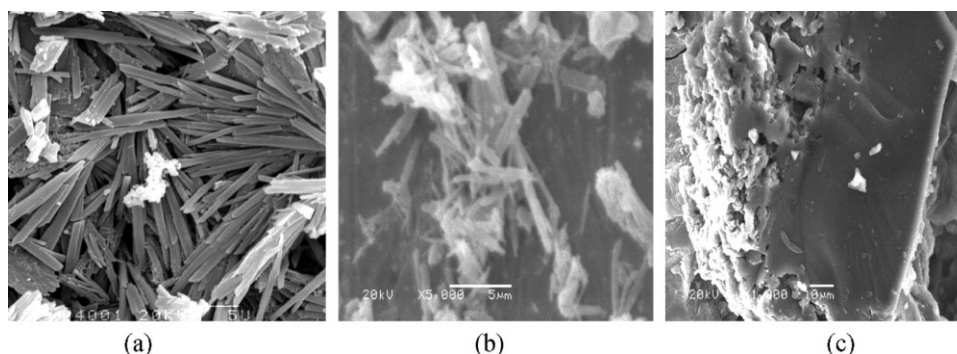
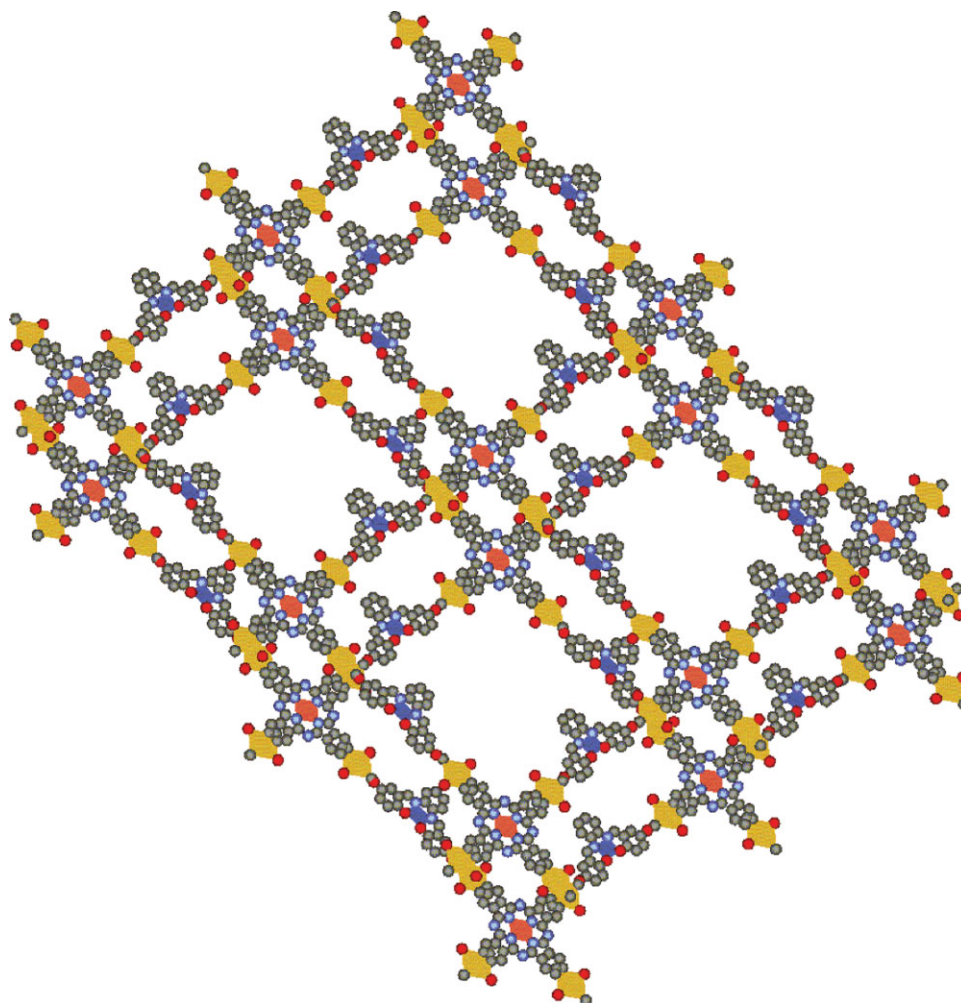


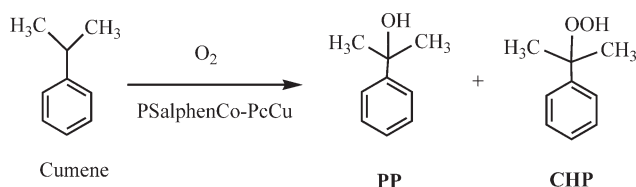
Figure 3 SEM images of the polymeric complex and the monomer (a) Co(diOHSalphen); (b) CuPc; (c) PSalphenCo-PcCu).



Scheme 2 Typical layer-structure of PSalphenCo-PcCu consists of two layer of sheet polymeric metal complexes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

is bigger than that of monomers (crystal size: about 2–8 μm), the hole in each polymer layer is big enough, whose diameters are more than 3 nm as shown in Scheme 2. Therefore, substrate (diameter <1 nm) can easily penetrate through surface layer and be catalytic oxidized in inner layer, which is partly similar to active center of enzymes.²⁷ It is also suggested that holes in the polymer layer are benefit to selectivity.

The oxidation of cumene with molecular oxygen was performed without any solvents or additional additives. The selectivity of products in the period



Scheme 3 Aerobic oxidation of cumene catalyzed by PSalphenCo-PcCu.

of the catalytic oxidation was investigated (Fig. 4). It showed that accompanying with conversion of cumene, the contents of CHP gradually increased when the contents of PP slowly varied. The relative concentration of CHP increased from 0 to 95%, but the relative concentration of PP has a few variations.

The effects of temperature, catalyst amount, and reused time on the catalytic oxidation of cumene by

TABLE I
Aerobic Oxidation of Cumene Catalyzed by PSalphenCo-PcCu and Its Monomers

Catalyst	Conversion (%)	Selectivity (%)	
		PP	CHP
Co(di-OHSalphen)	64	10	80
CuPc	45	15	82
PSalphenCo-PcCu	76	9	89

Conditions: Cat. 1 mg, cumene 2 mL, 1 atm of O₂, 8 h at 100°C.

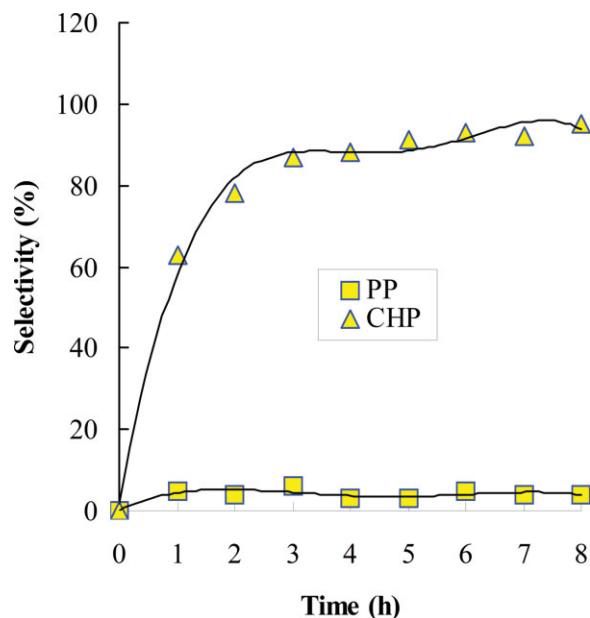


Figure 4 The relationship between aerobic oxidation products distribution with reaction time. Cond: Cat. 1.5 mg, cumene 2 mL, 1 atm of O₂, at 100°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the polymer complex (PSalphenCo-PcCu) were investigated.

Effect of reaction temperature

The influence of reaction temperature on catalyst activity of PSalphenCo-PcCu was investigated. Figure 5 reveals that the catalytic activity of PSalphenCo-PcCu increased with reaction temperature. The optimum temperature is 100°C. And the conversion of

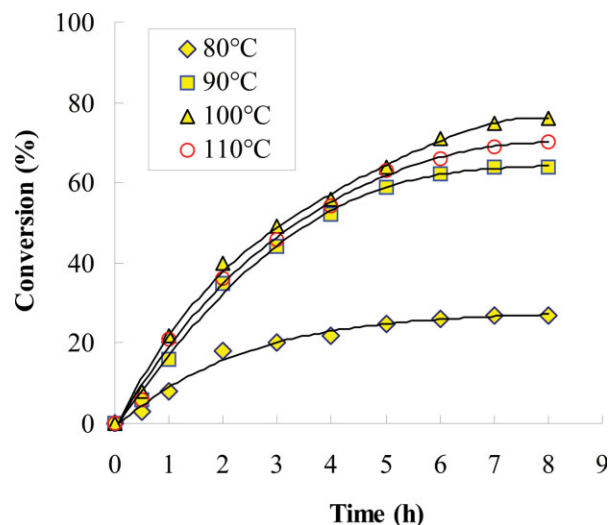


Figure 5 The influence of temperature on aerobic oxidation of cumene catalyzed by PSalphenCo-PcCu. Cond: Cat. 1 mg, cumene 2 mL, 1 atm of O₂. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

cumene decreases when reaction temperature is more than 100°C.

Effect of catalyst amount

The oxidation was carried out at 100°C by varying the amount of catalyst. The results are shown in Figure 6. It indicates that the catalytic activity of PSalphenCo-PcCu increase with the amount of the catalyst increasing, and the catalytic activity is the highest when amounts of the catalyst and substrate are 1.5 mg and 2 mL, respectively. It shows that its catalytic activity decreased if the amount of catalyst is too low. However, when the catalyst amount is

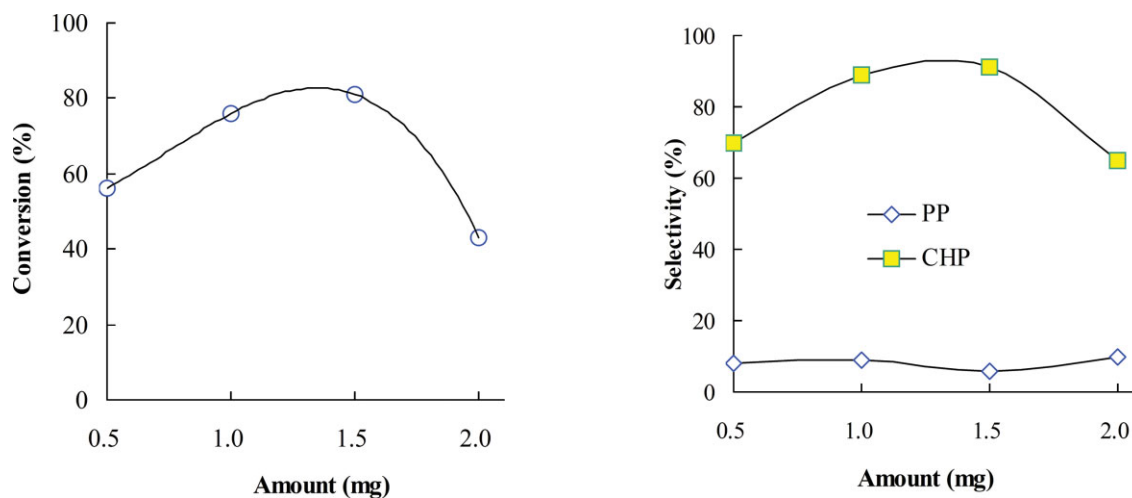


Figure 6 The effect of catalyst amount on aerobic oxidation of cumene catalyzed by PSalphenCo-PcCu. Cond: Sub. 2 mL, 1 atm of O₂, 8 h at 100°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

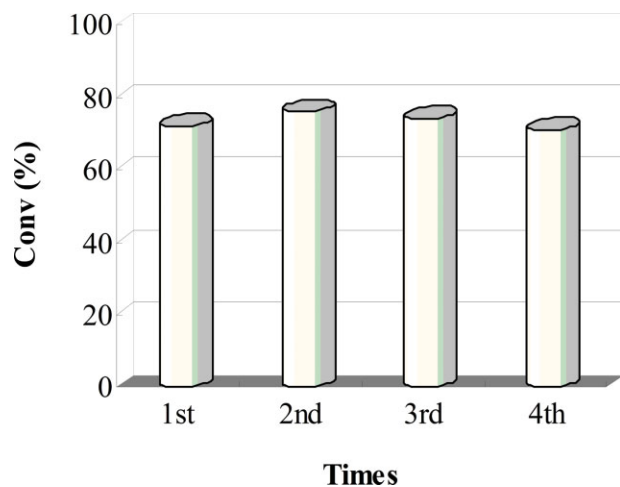


Figure 7 Reusability of PSalphenCo-PcCu on catalytic aerobic oxidation of cumene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

too high, it also inhibits oxidation reaction. As the sheet polymer metal complex belongs to porous polymer, it is suggested that the products or active intermediates of aerobic oxidation should have been absorbed into holes of polymer layers when the amount is too much, which inhibits oxidation reaction.

The recycle ability of PSalphenCo-PcCu

The recycle ability of PSalphenCo-PcCu has also been measured. As shown in Figure 7, the catalytic activity of PSalphenCo-PcCu remained until the fourth circle.

CONCLUSIONS

Polymeric Salphen Schiff base-phthalocyanine Co-Cu dinuclear metals complex was prepared successfully by interfacial condensation polymerization with Co(diOHSalphen) and [CuPc(SO₂Cl)₄] for the first time. Cumene was employed to investigate its catalytic activity in activation of molecular oxygen. In the presence of PSalphenCo-PcCu, conversion of cumene and total selectivity of oxidation products

were up to 76 and 98%, which better than two monomer [Co(diOHSalphen) and CuPc].

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