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# Preparation of Co-Na Heterobinuclear Polymeric Complex of Salen-Crown Ether and its Catalytic Activation for Molecular Oxygen

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*The Co-Na heterobinuclear polymer complex based on Salen Schiff base and crown ether have been prepared by a method of interfacial polymerization without the presence of a phase transfer catalyst. The catalytic behavior of the Co-Na heterobinuclear polymer complex in aerobic oxidation of cyclohexene has been studied.*

**Keywords** heterobinuclear, activation, dioxygen

## Introduction

Crown ethers and Salen Schiff base are two important groups of ligands extensively studied with respect to their high affinity to alkali and transition metal ions, respectively. They play important roles in catalytic and material science.<sup>[1–10]</sup> We found that the polymeric porphyrin metal complexes have more stability and activity in catalytic activation for molecular oxygen,<sup>[11]</sup> whose purpose is mild catalytic aerobic oxidation of hydrocarbon with an environment friendly process. However, the cost of porphyrin is high. It was also found that Schiff base complexes are an effective catalyst for aerobic oxidation of olefins.<sup>[12]</sup> The core of Salen Schiff base with N,N,O,O-coordination is easier to be synthesized than that of porphyrin. Therefore, the complexes of Salen Schiff base are more attractive. Recently, some compounds composed of multifunctional ligands, carrying both a hard and soft donor site such as crown ethers together with Salen moiety, have been reported.<sup>[13–15]</sup> To our knowledge, very few studies were carried out on the synthesis of a heterobinuclear polymer complex based on Salen Schiff base and crown ethers.<sup>[16]</sup> In this paper, a new type of Co-Na heterobinuclear polymer complex was

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prepared and its catalytic properties in the aerobic oxidation of cyclohexene have also been investigated.

The structure of the monomer and Co-Na heterobinuclear polymer complex (P-SalPhen-dSdB18C6- (Co-Na)) is shown in Sch. 1.

## Experimental

### Materials

Both dibenzo-18-crown-6 and 2,4-dihydroxybenzaldehyde were obtained from Aldrich-Chemical. Cyclohexene was purified by fractionating distillation just before use. Other reagents and metals salts were available commercially.

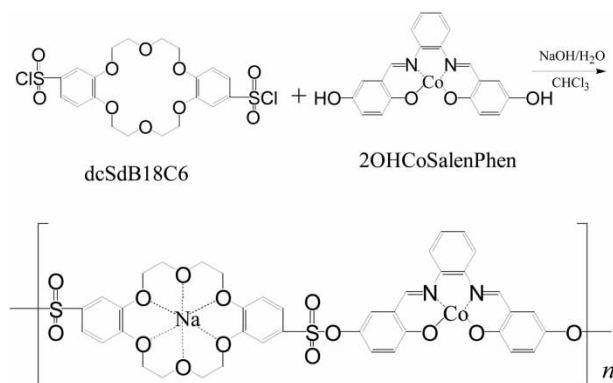
### Analyses and Physical Measurements

IR spectra were recorded in KBr disks with a Alpha-centauri FT-IR spectrophotometer. XPS (small area x-ray photoelectron spectroscopy) data were recorded with the PHI-5702 Multi-Technique System, Power Source By  $MgK_{\alpha}$  line and Ag  $3d_{5/2}$  FWHM  $\leq 0.48$  eV. The thermal analysis was recorded on a Shimadzu DT-40 Thermal Analyzer ( $10^{\circ}C/min$ ). A scanning electron micrograph (SEM) was obtained using a Hitachi S-450 scanning electron microscope. The reaction products of oxidation were determined and analyzed by a Shimadzu GC-16A gas chromatograph, QP-1000A GC/MS system.

### Synthesis of Monomer and Polymeric Complexes

The 2OHCosalenPhen was synthesized using  $Co^{2+}$  as a template by 2,4-dihydroxybenzaldehyde and *o*-phenylene-diamine (2 : 1) in propanol protected by nitrogen at  $70^{\circ}C$  for 8 h with a yield of 80%.

Dichlorosulfonated-dibenzo-18-crown-6 (dcSdB18C6) was synthesized from dibenzo-18-crown-6.<sup>[17]</sup> The  $HSO_3Cl$  was added dropwise to the chloroform solution of Dibenzo-18-crown-6 under an atmosphere of argon and cooled in an ice-bath. After stirring at room temperature for 8 h, the reaction mixture was poured into ice. Then, the



**Scheme 1.** Structure of P-SalPhen-dSdB18C6(Co-Na).

organic phrase was dried by  $\text{CaCO}_3$ . After filtering, the filtrate was evaporated under vacuum to dryness and recrystallized from ethyl acetate/acetonitrile to provide a white powder with a yield of 54%.

The P-SalPhen-dSdB18C6(Co-Na) was synthesized using interfacial polymerization. Due to the phase transfer ability of the crown ether, the condensation polymerization and complex reaction occurred at the same time without the presence of phrase transfer catalyst, in a high reaction rate. The chloroform solution of dichlorosulfonated-dibenzo-18-crown-6 was added dropwise into aqueous 2OHCoSalenPhen with sodium hydroxide and sharply stirred. After a reaction for 2 h at room temperature, the crude product was isolated as only a solid by filtration, and washed separately with  $\text{H}_2\text{O}$  and acetone. The black copolymer complex was obtained with a yield of 86% after drying under vacuum.

## Results and Discussion

### Preparation and Characterization

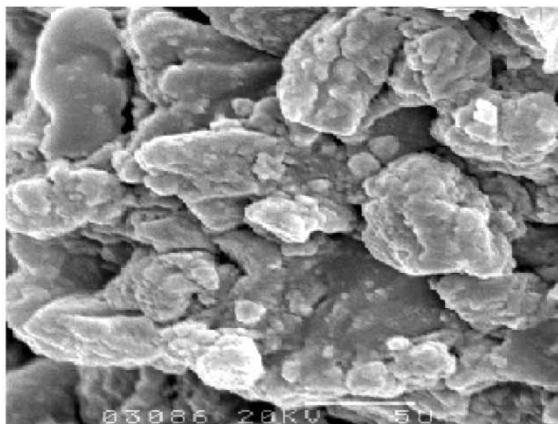
In order to find the influence of alkali metal ions for interfacial polymerization, we tried to synthesize polymer heterobinuclear complexes in LiOH. However, the polymer cannot be obtained under the same conditions.

The IR spectra of P-SalPhen-dSdB18C6(Co-Na) were measured and compared with the monomer. The absorption of S=O double bond of symmetrical stretching vibration is near  $1181\text{ cm}^{-1}$ , and the asymmetrical stretching vibration is near  $1364\text{ cm}^{-1}$ . The stretching vibrations of C=N and Ph-O bond appear at  $1613\text{ cm}^{-1}$  and  $1226\text{ cm}^{-1}$ . The weak absorption at  $463\text{ cm}^{-1}$  and  $504\text{ cm}^{-1}$  attributed to the Co-N bond and Co-O bond, respectively. The  $-\text{CH}_2-\text{O}-\text{CH}_2-$  absorption peak shifts from  $1143\text{ cm}^{-1}$  to  $1113\text{ cm}^{-1}$  indicates that sodium ion is coordinated to oxygen in crown ether. The data of XPS of the compounds are shown in Table 1. Compared with 2OHCoSalenPhen, the binding energy of cobalt of P-SalPhen-dSdB18C6(Co-Na) is shifted slightly (0.4 eV) to low energy for its special polymer framework and crown ether moiety.<sup>[18]</sup>

The polymer complex cannot be soluble in water and general organic solvents except being slightly partly soluble in DMF. The morphologies and surface image of the P-SalPhen-dSdB18C6(Co-Na) is further examined with scanning electron microscopy (SEM). Figure 1 reveals the surface image of the polymer Co-Na heterobinuclear complex. The compound has also been characterized by thermal analysis, which showed that the polymer is decomposed above  $250^\circ\text{C}$ .

**Table 1**  
XPS data of  $\text{Co}(\text{OAc})_2$ , 2OHCoSalenPhen, and P-SalPhen-dSdB18C6(Co-Na)

| Compound                   | Binding energy (eV) |                    |                    |                     |
|----------------------------|---------------------|--------------------|--------------------|---------------------|
|                            | $\text{C}_{1s1/2}$  | $\text{O}_{1s1/2}$ | $\text{N}_{1s1/2}$ | $\text{Co}_{2p3/2}$ |
| $\text{Co}(\text{OAc})_2$  | —                   | —                  | —                  | 779.6               |
| 2OHCoSalenPhen             | 284.8               | 532.4              | 399.3              | 781.2               |
| P-SalPhen-dSdB18C6 (Co-Na) | 284.8               | 532.9              | 399.4              | 780.8               |



**Figure 1.** The scanning electron microscopy (SEM) of the P-SalPhen-dSdB18C6-(Co-Na).

### *Catalytic Activity*

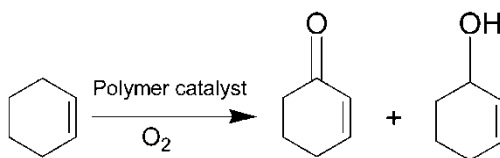
In order to investigate catalytic activation properties for molecular oxygen by P-SalPhen-dSdB18C6(Co-Na), the aerobic oxidation of cyclohexene was studied. The reaction was carried out in 1 atm of O<sub>2</sub> at 70°C. In the presence of a trace of HOAc, the reaction mainly takes place on the allyl carbon of the cyclohexene (Sch. 2), which give corresponding ketone and alcohol.

Compared with the monomer of Salen Schiff base (2OHCosalenPhen), the Co-Na heterobinuclear polymer complex (P-SalPhen-dSdB18C6(Co-Na)) shows higher activity and stability. It is suggested that the crown ring helps to increase catalytic activity, and the polymer skeleton increases stability.

The influence of an additive to catalytic activity and product selectivity was investigated. When HOAc was added into the reaction system, the conversion of cyclohexene increased from 58.1% to 92.4% and the selectivity of alcohol increased from 39.7% to 62.4%. In addition, the ration of the epoxide and hydroperoxide was noticeably decreased to barely detectable. On the contrary, when the organic base, pyridine, was added into catalytic oxidation system, the reaction stopped.

### **Conclusions**

The Co-Na heterobinuclear polymer complex based on Salen Schiff base and crown ether was successfully synthesized using the methods of template and interfacial polymerization. The complex, for its special framework and crown ether moiety, shows high catalytic activity and selectivity for oxidation of cyclohexene with molecular oxygen under mild conditions.



**Scheme 2.**

## Acknowledgment

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18. According to the XPS data. Compared to the binding energy of Na of NaCl, the chemical shift of that of SalPhen-DcsDbC-(Co<sup>II</sup>-Na<sup>+</sup>) is about 1.0 eV from 1072.5 to 1071.5 eV.