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Oxidation of Styrene with Molecular Oxygen Catalyzed by Polymer-Supported O-Aminobenzoic Acid Salicylaldehyde Schiff-Base Copper(II) Complex

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Schiff-base complexes of copper supported on chloromethylated polystyrene as a catalyst have been studied in the oxidation of styrene with molecular oxygen. The main products are benzaldehyde and the epoxide of styrene. Compared with the unsupported copper complex, the polymer supported complex has more effective catalytic activity, and could be easily separated and reused. The influences of reaction temperature and the amount of catalyst have also been investigated.

Keywords chloromethylated polystyrene, supported copper Schiff-base, catalyst, styrene, benzaldehyde, epoxide of styrene

Introduction

Transition metal complexes as catalysts for epoxidation of olefin have attracted a great deal of attention in recent years (1–3). In general, selected ligands include porphyrin derivatives, macrocyclic polyamines, and Schiff bases (3–5). During the process of catalytic reaction, these catalysts need a mono-oxygen source such as H_2O_2, PhIO, NaClO, etc., to carry out oxygen transferring to the olefin. However, the method has two disadvantages. Firstly, catalysts are not easily separated from reaction mixtures and cannot be used repeatedly. Secondly, dealing with these oxidants mentioned above is not environmentally friendly. To make these useful catalysts recyclable and economical while preserving their catalytic efficiency, researchers have synthesized polymer supported transition metal complexes for epoxidation of olefins (6–8). At the same time, molecular oxygen is employed as a convenient oxidant. Compared with above-mentioned oxidants, molecular oxygen is abundant, easy to handle, and is less harmful to the environment. However, when molecular oxygen is used as an oxidant, aldehydes or cyclic ketone are added in the reaction system as reductant in order to assist completing the reaction (9–11). For example, the oxidation of styrene, catalyzed with Schiff-base

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nickel or cobalt complexes, O_2 is applied as oxidant and isobutyl aldehyde as reductant. During the process, the epoxide of styrene was produced and isobutyl aldehyde was also transformed to carboxylic acid (12). As the aldehyde and cyclic ketone as reductant influenced the formation and selectivity of products, we intended only to use molecular oxygen as oxidant. In this work, we prepared chloromethylated polystyrene supported Schiff-base metal complexes, where the metal is copper, cobalt, nickel, manganese and iron, respectively. In the oxidation of styrene using molecular oxygen catalyzed with these complexes, the products were the epoxide of styrene and benzaldehyde, and are different from the literature (13). Furthermore, comparing the catalytic property of supported with unsupported complexes, polymer supported Schiff-base metal copper complexes have better catalytic activity.

Experimental

Reagents

Chloromethylated polystyrene (containing 5.7 mmol of Cl/g of resin and 2% of crosslinked divinybenzene), *o*-aminobenzoic acid, salicylaldehyde, anhydrous ethanol, styrene and metallic salt were obtained commercially. Solvents were purified before use.

Instruments

IR spectra were recorded in KBr on an Alpha-Centauri FT-IR spectrophotometer (Shimadzu, Japan). XPS (small area X-ray photoelectron spectroscopy) data were recorded with the PHI-5702 Multi-Technique System (PHI, U.S.A.), the power source was a MgK_α line, and the $Ag_{3d5/2}$ full width at half-maximum was less than or equal to 0.48 eV. Elemental analysis was performed on a Itali Carbo-Erba 1106 elemental autoanalyzer (Carbo-Erba, Italy). The content of metal was obtained by using ARL-3520 inductively coupled plasma (ICP) instrument (TJA, U.S.A.). The reaction products were analyzed on Shimadzu QP-1000A gas chromatography/mass spectrometry (GC/MS) system (Shimadzu, Japan), and a GC-16A gas chromatography (Shimadzu, Japan). The differential thermal analysis (DTA) was measured on a Shimadzu DT-40 thermal analyzer.

Preparation of Polymer-Supported Schiff-Base Ligand (PS-H_2L)

The Schiff-base ligand (H_2L), formed from *o*-aminobenzoic acid and salicylaldehyde, was synthesized according to the documented procedure (14). The structure was confirmed by elementary analysis and IR spectra.

Thus, chloromethylated polystyrene (5.0 g) was added to acetone (20 ml) and was allowed to stand for 30 h. To this acetone solution, Schiff-base ligand (4.8 g) was added followed by triethylamine (0.5 g). The mixtures were heated under reflux for 30 h. After being cooled, the polymer precipitated out which was filtered and washed, respectively, with water and anhydrous ethanol. Then, the solid was dried in vacuum at room temperature for 24 h.

General Method for the Synthesis of PS-H_2L-Cu Complex

The polymer-supported Schiff-base ligand (PS-H_2L) (0.8 g) was allowed to swell in anhydrous ethanol (30 ml) for 1 h. According to $N/Cu = 1:1$ (mol/mol), the specified amount of $Cu(Ac)_2 \cdot 2H_2O$ was added to the above suspension. The mixture was heated at 313 K for 36 h with stirring and then cooled to room temperature. The green resin was filtered, washed with ethanol, and dried in vacuum.

Other polymer-supported Schiff-base metal complexes, where the metal is cobalt, nickel, manganese and iron were prepared in the same way.

The formation of chloromethylated polystyrene with Schiff-base complex is shown in Scheme 1.

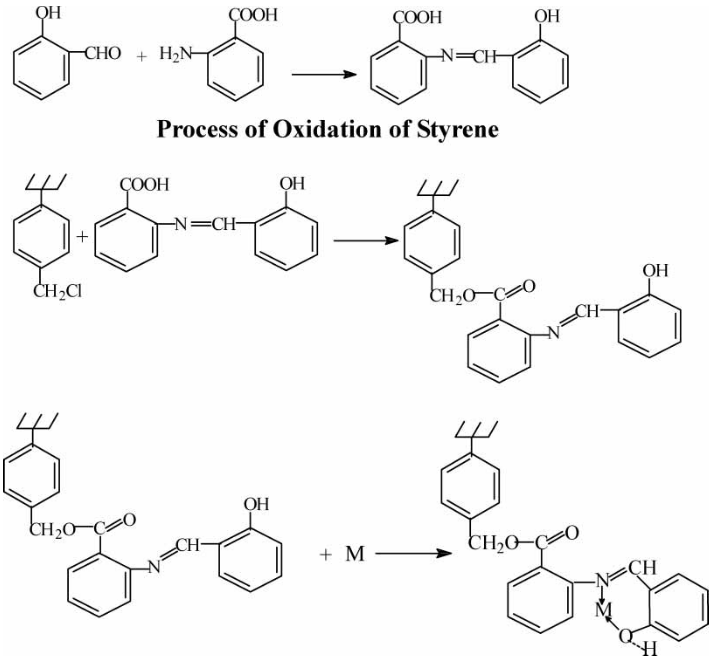
Process of Oxidation of Styrene

Oxidation of styrene was carried out according to the literature (15). After styrene and PS-H_2L-Cu were added to the reactor with a gas outlet tube, the oxygen was repeatedly exchanged in order to fill the glass reactor. The mixture was heated to about 343 K in an oil bath and stirred with a magnetic stirrer. The volume of oxygen consumed was measured from the burette. The products were benzaldehyde and epoxide of styrene, which were analyzed on a Shimadzu QP-1000A GC/MS system and GC-16A model (Figure 1).

Results and Discussion

Characterization

In IR spectra (data listed in Table 1), the band at 1635 cm^{-1} is due to the $\gamma_{C=N}$. In the polymer-supported complex, this band undergoes a negative shift by 24 cm^{-1} indicating the involvement of nitrogen atom of the azomethine in coordination (12). The polymer



Scheme 1. The formation of polymer supported complex.

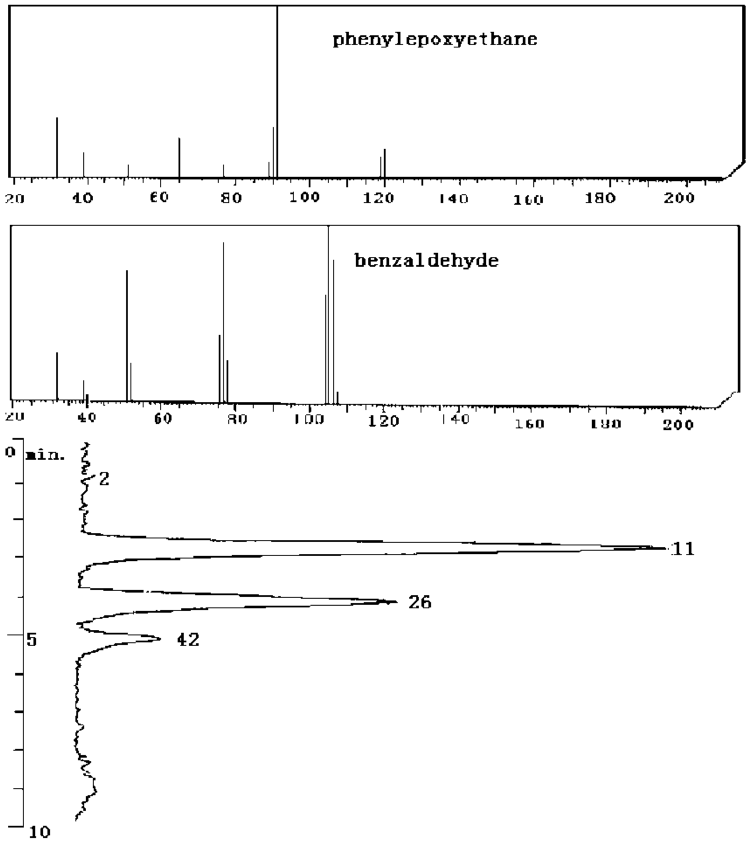


Figure 1. GC/MS spectra of the oxidation products of styrene.

ligand (PS-H_2L) shows a band at 1534 cm^{-1} due to the ν_{C-O} (phenolic) and this band undergoes a positive shift of 7 cm^{-1} in PS-H_2L-Cu. This is indicative of the coordination of copper ion with phenolic oxygen atom of the ligand. And the polymer-supported complex shows two new bands at 424 and 344 cm^{-1} due to the Cu-O and Cu-N, respectively.

Table 1
ICP and IR spectra data of complexes

Compound	MC^a	Wavelength (cm^{-1})					
		ν_{asCOO}	ν_{sCOO}	ν_{C-O}	$\nu_{C=N}$	ν_{O-M}	ν_{N-M}
PS-H_2L	—	1600	1429	1250	1635	—	—
PS-H_2L-Co	1.7	1595	1408	1237	1610	419	354
PS-H_2L-Ni	5.3	1594	1403	1234	1612	425	361
PS-H_2L-Cu	2.8	1590	1429	1234	1611	424	344
PS-H_2L-Mn	3.8	1590	1407	1236	1614	412	334
PS-H_2L-Fe	2.6	1592	1406	1234	1611	420	319

MC^a: metal content (10^{-2} mmol/g).

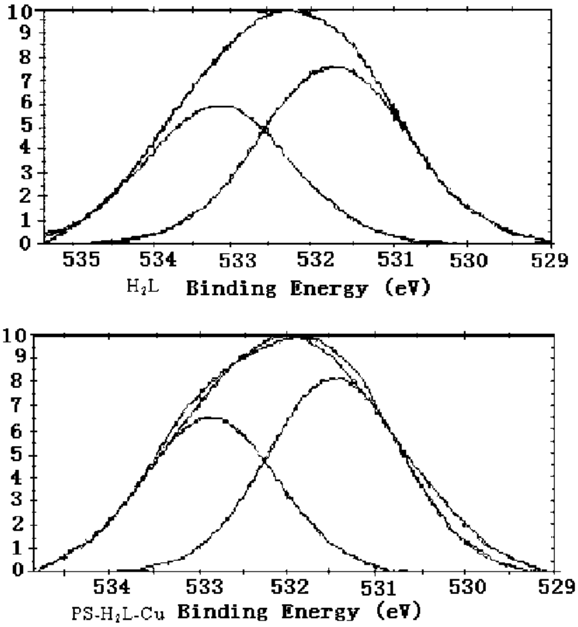


Figure 2. Resolved O_{1s} XPS spectrum of H_2L and PS-H_2L-Cu.

In order to prove the coordination of polymer-supported Schiff-base ligand with copper ion, corresponding small area X-ray photoelectron spectroscopy of copper acetate, ligand and its complex have been studied (Figure 2 and Table 2). Compared with that of copper acetate, the binding energy of $Cu_{2p3/2}$ of complex increases 3.2 eV. The change of binding energy of the $Cu_{2p3/2}$ means a decrease of its election density. Binding energy of $N_{1s1/2}$ of the polymer complex decreases 0.6 eV than that of the corresponding ligand of H_2L. The electronic state of the nitrogen atom in the polymer complex is of higher electron density and, therefore, the electrons in the copper atom may flow into the nitrogen atom to form a N-Cu coordination bond. The oxygen peak in the complex could be divided into two peaks, of which one belongs to the oxygen atoms in phenolic group and the other belongs to the oxygen atom in carbonyl group. The binding energy of $O_{1s1/2}$ of the polymer complex is raised of 0.8 eV than that of the corresponding support, which indicates that only oxygen atom in phenolic group bound with metal

Table 2
XPS data

	Binding energy (eV)			
Compound	$C_{1s1/2}$	$O_{1s1/2}$	$N_{1s1/2}$	$Cu_{2p3/2}$
H_2L	284.6	531.2	400.2	—
PS-H_2L-Cu	284.6	532.0	399.6	935.0
$Cu(Ac)_2 \cdot 2H_2O$	—	—	—	931.8

Table 3
Oxidation properties of styrene with different catalysts

		Selectivity (%)	
Catalyst	Conversion (%)	Epoxide of styrene	Benzaldehyde
PS-H_2L-Ni	17.6	7.5	81.4
PS-H_2L-Co	30.8	9.7	74.9
PS-H_2L-Cu	64.8	29.7	60.5
PS-H_2L-Mn	53.2	18.6	71.4
PS-H_2L-Fe	13.7	6.8	80.9

Catalyst: 3 mg, substrate: 1 ml, temperature: 353 K, reaction time: 8 h.

ion. The structure of complex can be ensured as in Scheme 1. According to ICP, the copper content is 0.028 mmol/g catalyst (Shown in Table 1).

Catalytic Activity of Different Metal Complexes

The properties of metal complexes as catalysts in the oxidation of styrene with oxygen were determined and the results are shown in Table 3. Under the same reaction conditions, all polymer-supported Schiff-base metal complexes possess catalytic activity, but the copper complex has the highest catalytic ability. So, choosing it as a target, we investigated the catalytic properties in the oxidation of styrene with molecular oxygen systematically.

Effect of Support on Catalytic Activity

From Figure 3, in comparison with the unsupported Cu(II) Schiff-base, the polymer supported ones have more effective catalytic activity for the oxidation of styrene with

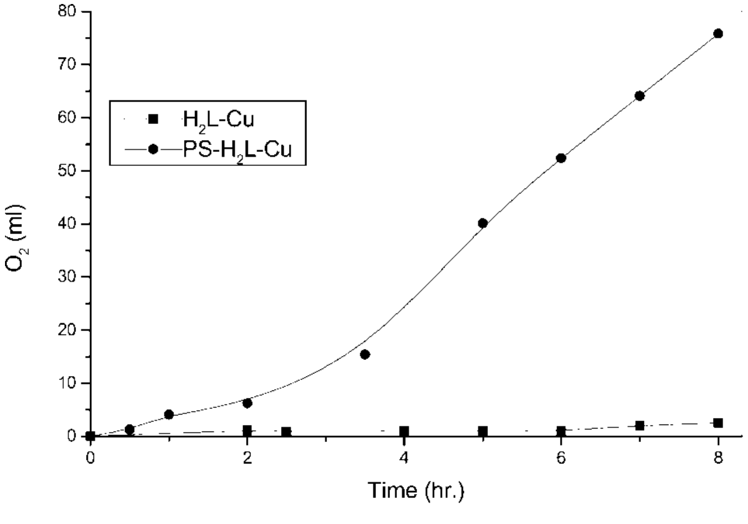


Figure 3. The consumption of oxygen of supported and unsupported Schiff-base copper complexes. Catalyst: 3 mg; styrene: 3 ml; temperature: 353 K.

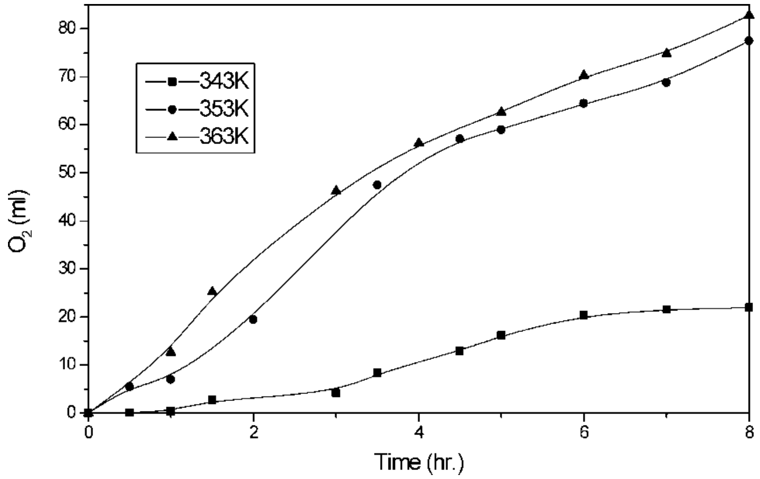


Figure 4. The relationship of consumption of O_2 and the reaction time on various temperature. Catalyst: 1 mg; styrene: 1 ml; reaction time 8 h.

molecular oxygen. For PS- H_2L-Cu, the consumption of oxygen increased quickly and the conversion of styrene was 17.0 times more than that of unsupported complexes. Furthermore, the epoxide of styrene is produced in the catalytic oxidation with polymer supported catalysis. Therefore, polymer support with H_2L-Cu is more likely to be effective.

Effect of Temperature on Catalytic Activity

The catalytic activity of PS-H_2L-Cu was investigated as a function of temperature at 343 K, 353 K and 363 K, respectively. The consumption of oxygen with 1 mg of PS-H_2L-Cu is shown in Figure 4. It is clear that the higher reaction temperature, the shorter the induction period. The consumption of oxygen also increases with the increasing temperature. The product analysis shows that besides benzaladehyde, there is epoxide of styrene. The conversion of styrene and selectivity of products are collected in Table 4,

Table 4
The conversion of styrene and the selectivity of products at different temperature

		Selectivity (%)	
Temp. (K)	Conv. (%)	Ph-CHO	Ph-EXO
343	9.0	94.6	4.6
353	39.4	50.8	19.1
363	39.7	51.0	27.9

Catalyst: 2 mg, substrate: 1 ml, reaction time: 8 h.

Table 5
The conversion of styrene and the selectivity of products with the different amounts of catalyst

		Selectivity (%)	
Catalyst (mg)	Conv. (%)	Ph-CHO	Ph-EXO
1.0	39.7	51.0	17.9
2.0	39.3	50.7	19.1
3.0	36.7	46.1	29.7
4.0	34.7	36.7	37.1

Substrate: 1 ml, temperature: 353 K, reaction time 8 h.

the conversion of styrene at 363 K is 4.2 times greater than that of 343 K, and the selectivity of epoxide is also increased nearly 4.0 times.

Effect of the Amount of Catalyst on Catalytic Activity

At 363 K, the results of oxidation of styrene in the presence of various amounts of PS-H_2L-Cu are shown in Table 5. When the amount of catalyst increases from 1.0 mg to 4.0 mg per 1 ml of styrene, the conversion of styrene decreases from 39.7% to 34.7%. Therefore, a larger amount of catalyst lowers the conversion. However, the selectivity of epoxide of styrene increases with an increasing amount of catalyst. There is an increase of 2.1 times in selectivity of epoxide when the amount of catalyst is increased 10 times.

Recycling of Catalyst

Oxidation of styrene using 2 mg of catalyst was recycled 3 times and the results are shown in Table 6. The conversion of styrene is almost unchanged. It shows that the catalyst is stable at 363 K, and the metal ion is not washed away in the reaction process. Thus, the catalyst can be reused many times. In contrast, the low molecular weight complexes are completely destroyed during the first run and changed color, while it is active in the first cycle.

Table 6
Recycle experiments

		Selectivity (%)	
Cycling times	Conv. (%)	Ph-CHO	Ph-EXO
1	39.6	50.5	19.3
2	38.2	49.0	17.3
3	39.4	49.9	20.2

Catalyst: 2 mg, temperature: 353 K, Substrate: 1 ml, reaction time 7 h.

Conclusions

For oxidation of styrene, PS-H_2L-Cu is a very effective catalyst. It is superior to unsupported H_2L-Cu, PS-H_2L-Cu as a catalyst, and possesses the following desirable properties: (1) catalytic ability is higher; (2) it is stable at 363 K; (3) the catalysts are easily separated from the reaction systems and could be reused many times. When the catalyzed reaction is carried out at high temperature or in the presence of large amount of catalysts, the selectivity for the epoxide of styrene increases.

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