Synthesis and Catalytic Oxidation Properties of Polymer-Bound Cobalt Complexes

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ABSTRACT: Polymer-bound 2,2′-bipyridine cobalt complexes PSBPY-Co, PSBPY-Co-bipy, PSBPY-Co-oxine, and PSBPY-Co-phen (where PSBPY: polystyrene bound-2,2′-bipyridine; bipy: 2,2′-bipyridine; phen: 1,10-phenanthroline) were synthesized and investigated by IR, X-ray photoelectric spectroscopy, thermogravimetry–differential thermal analysis, inductively coupled plasma atomic emission spectrometry, and elemental analysis. The complexes were found to be catalysts for the oxidation of alkylbenzenes and cyclohexene in the presence of molecular oxygen in the absence of solvent. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1068–1074, 2000

Key words: polymer-bound cobalt complexes; catalysts; alkylbenzenes; cobalt complexes; cyclohexene; catalytic oxidation

INTRODUCTION

Transition metal complex catalyzed oxidation of organic substrates is a topic of current research.[1–8] Cobalt complexes have received much attention recently due to the potential application of these complexes as oxidation catalysts for the oxidation of cyclic althenes, enolizable aldehydes, secondary alcohols, and other organic substrates.[9–14] Previously we reported the synthesis and catalytic properties of a series of polymer-bound iron, copper, and ruthenium complexes.[15–18] We described here the synthesis, investigation, and catalytic oxidation properties of polymer-supported 2,2′-bipyridine cobalt complexes PSBPY-Co (**1**), PSBPY-Co-bipy (**2**), PSBPY-Co-oxine (**3**), and PSBPY-Co-phen (**4**; where PSBPY: polystyrene-bound 2,2′-bipyridine, bipy: 2,2′-bipyridine, and phen: 1,10-phenanthroline). The charge change on the cobalt atoms in cobalt complexes is different from that on the iron, copper, and ruthenium atoms in the corresponding complexes previously reported.[15–18] The catalytic oxidation of toluene, *p*-chlorotoluene, *o*-nitrotoluene, ethylbenzene, *n*-propylbenzene, iso-propylbenzene, and cyclohexene were carried out under 1 atm of molecular oxygen at 110 or 70°C without the use of any solvent or coreductant, affording corresponding ketones (or aldehydes) and alcohols. The complexes were stable in air and can be reused. They were very convenient for ready separation. The influence of catalysts on the oxidation reactions was also discussed.

EXPERIMENTAL

Materials

All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise; toluene, *p*-chlorotoluene, *o*-nitrotoluene, ethylbenzene, *n*-propylbenzene, iso-propylbenzene, and cyclohexene were distilled before the reaction. Linear-polystyrene (MW 130,000–150,000) bound 2,2′-bipyridine (PSBPY) was pre-

Table I   Element Analytical Data of Complexes (wt %)

Compound	C	H	N	Co
PSBPY	78.53	6.59	7.40	0
PSBPY-Co	61.95	5.49	3.17	15.96
PSBPY-Co-oxine	72.79	5.05	6.40	8.80
PSBPY-Co-bipy	83.63	6.39	4.96	3.20
PSBPY-Co-phen	84.76	6.21	5.22	2.95

pared in the general procedure based on the method previously described.[15] The nitrogen content of PSBPY was 7.40%.

Preparation of PSBPY-Co-L (Where L: 0; 2,2′-bipyridine; 1,10-phenanthroline and Oxine) Complexes

Polymer-bound cobalt complexes PSBPY-Co (**1**) PSBPY-Co-bipy (**2**), PSBPY-Co-oxine (**3**), and PSBPY-Co-phen (**4**) were synthesized in the following procedure: cobalt acetate $Co(Ac)_2 \cdot 4H_2O$ (0.25 g, 1.0 mmol), polymer-bound 2,2′-bipyridine PSBPY (0.3 g, N = 1.59 mmol), and low molecular weight ligand L [where (**1**) L = 0; (**2**) L = 2,2′-bipyridine, 0.15 g, 0.96 mmol; (**3**) L = oxine,

Table II   X-Ray Photoelectron Spectroscopy Data for Polymer-bipy, $Co(Ac)_2$, and Complexes 1–4

Compound	XPS Peak	Bing Energy Eb (eV)	ΔEb (eV)
$Co(Ac)_2$	$Co(2p_{3/2})$	780.2	0.0
	N(1s)	0.0	0.0
PSBPY	$Co(2p_{3/2})$	0.0	0.0
	N(1s)	399.3	0.0
PSBPY-Co	$Co(2p_{3/2})$	780.9	+0.7
	N(1s)	397.3	−2.0
		399.5	
PSBPY-Co-bipy	$Co(2p_{3/2})$	781.3	+1.1
	N(1s)	397.5	−1.8
		399.6	
		400.3	
PSBPY-Co-oxine	$Co(2p_{3/2})$	781.2	+1.0
	N(1s)	397.7	−1.6
		398.8	
PSBPY-Co-phen	$Co(2p_{3/2})$	782.1	+1.9
	N(1s)	397.1	−2.2
		398.8	
		400.7	

0.26 g, N, 1.79 mmol; (**4**) L = 1,10-phenanthroline, 0.19 g, 0.95 mmol] were added to 40 mL of absolute ethanol and refluxed for 24 h. The resulting products were isolated by filtration, and were thoroughly washed with ethanol and dried in vacuum for 48 h at room temperature. The complexes were characterized using IR, X-ray photoelectric spectroscopy, inductively coupled plasma atomic emission spectrometry (ICP), thermogravimetric–differential thermal analysis (TG-DTA), and routine elemental analysis. The results were shown in Tables I and II, and Figures 1–4.

Oxidation Procedure

In general, 2 mg of catalyst and 5 mL of substrate were added to a glass reactor with a gas inlet tube connected to a gas burette and an oxygen storage rubber container, and a gas outlet tube that could be opened to the air. The mixture was heated to 110°C in an oil bath and stirred with a magnetic stirring bar, the volume of oxygen absorbed was measured from the burette. The products in the reacted mixture were analyzed on Shimadzu QP-1000A gas chromatography/mass spectroscopy (GC/MS) system and GL-16A gas chromatograph with a 3 m × 3 mm OV-17 column. The results were shown in Figures 5 and 6.
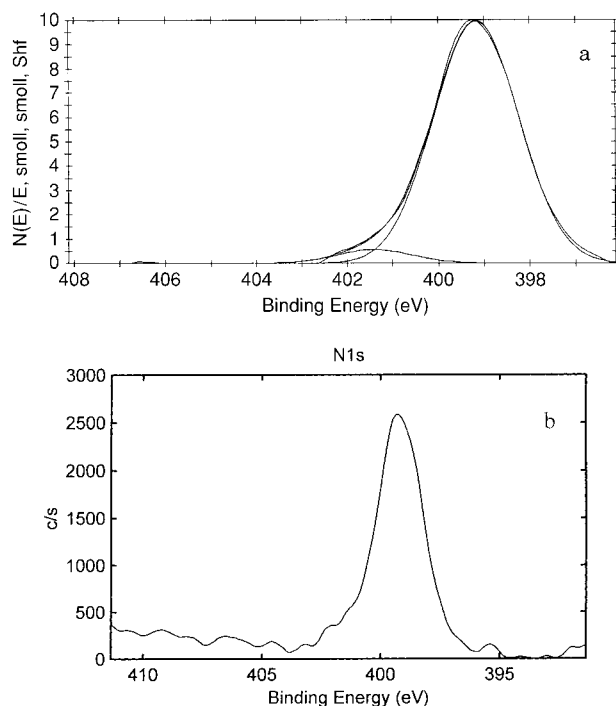

Figure 1   (a) Resolved N1s XPS spectrum of PSBPY and (b) N1s XPS spectrum of PSBPY.
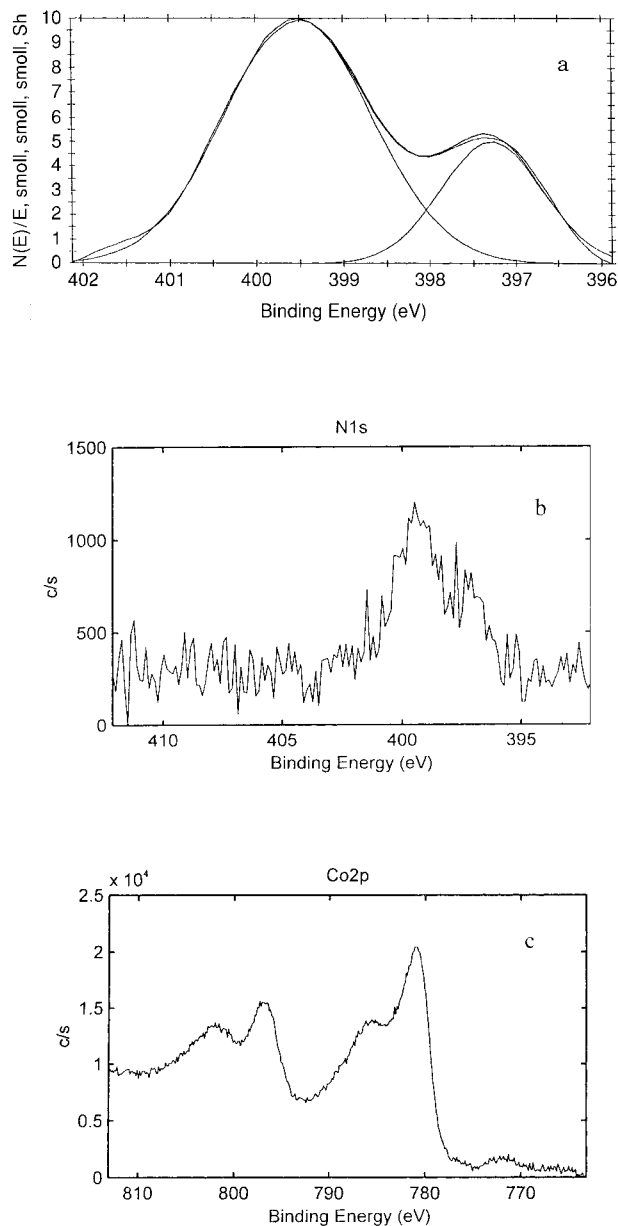
Figure 2 (a) Resolved N1s XPS spectrum of PSBPY-Co, (b) N1s XPS spectrum of PSBPY-Co, and (c) Co (2p$_{3/2}$) XPS spectrum of PSBPY-Co.
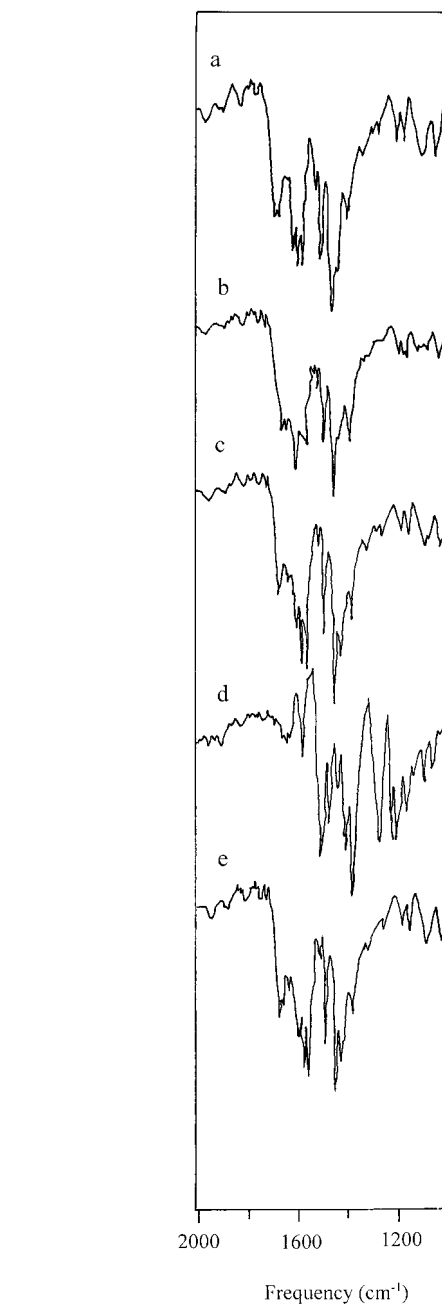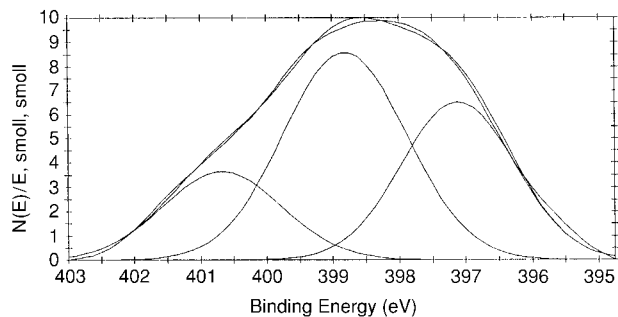

Figure 4 Infrared spectra of PSBPY (a), PSBPY-Co (b), PSBPY-Co-bipy (c), PSBPY-Co-oxine (d), and PSBPY-Co-phen (e).

RESULTS AND DISCUSSION

IR, XPS, and TG-DTA Characterization of Polymer-Bound Complexes

X-ray photoelectron spectroscopic (XPS) analysis was performed at room temperature on a PHI-500

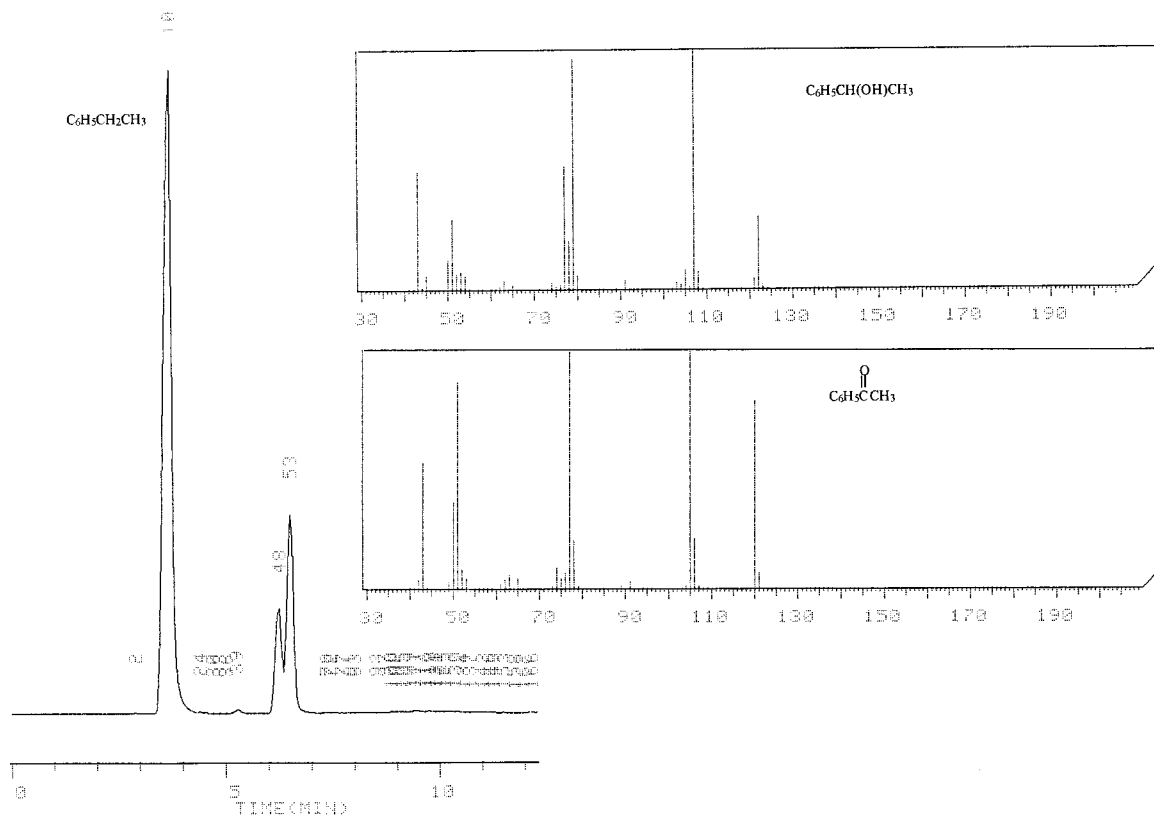**Figure 3** Resolved N1s XPS spectrum of PSBPY-Co-phen.

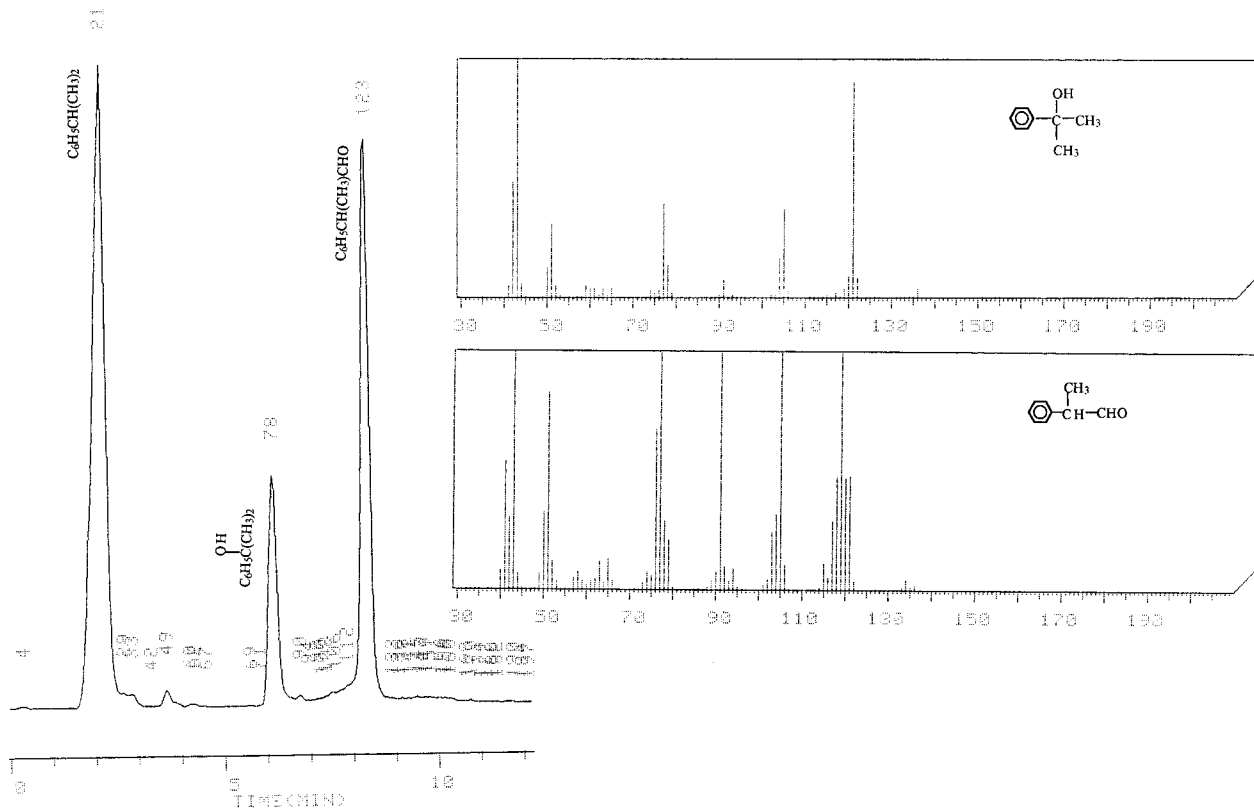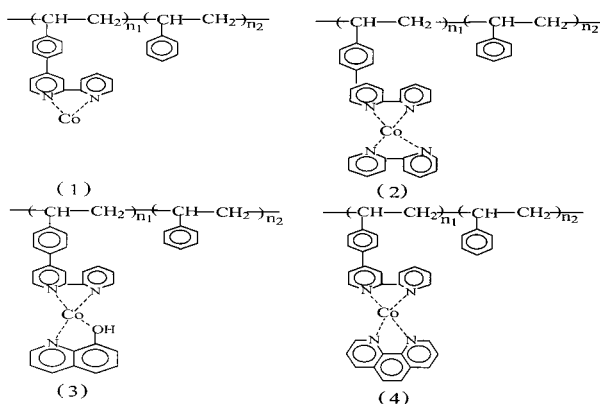**Figure 5**   GC/MS spectra of the oxidation products of ethylbenzene.

Figure 6   GC/MS spectra of the oxidation products of cumene.

Scheme 1 Suggested structure of PSBPY-Co (**1**), PSBPY-Co-bipy (**2**), PSBPY-Co-oxine (**3**), and PSBPY-Co-phen (**4**).

Figure 7 Effect of different catalysts (B, PSBPY-Co; C, PSBPY-Co-bipy; D, PSBPY-Co-oxine; and E, PSBPY-Co-phen) on the reactivity (Catalyst 2 mg; ethylbenzene 5 mL; 1 atm of O_2; 5 h at 110°C).

ESCA/SAM spectrometer using of Mg Kα radiation ($h\nu$ = 1254 eV). The typical X-ray power was 320 W. All XPS spectra were energy referenced to the C_{1S} photoemission peak at 284.6 eV. The $Co(2p_{3/2})$ and N(1s) binding energy data are shown in Table II. The $Co(2p_{3/2})$ binding energy is 780.9 eV in complex **1**, 781.3 eV in complex **2**, 781.2 eV in complex **3**, 782.1 eV in complex **4**, and 780.2 eV in cobalt acetate. Compared with that of cobalt acetate, the $Co(2p_{3/2})$ binding energies of the complexes **1–4** increased 0.7, 1.1, 1.0, and 1.9 eV, respectively. As shown in Figures 1 and 2, there is one N(1s) XPS peak in the resolved spectrum of the polymer-bound ligand PSBPY and two N(1s) XPS peaks in the resolved spectrum of complex PSBPY-Co. One peak corresponds to one N(1s) binding energy and two peaks correspond to two binding energies—one (399.5 eV) is almost equal to and the other (397.3 eV) is lower than that in the corresponding polymer-bound ligand PSBPY. This indicates that there are two components of nitrogen in the complex PSBPY-Co. The
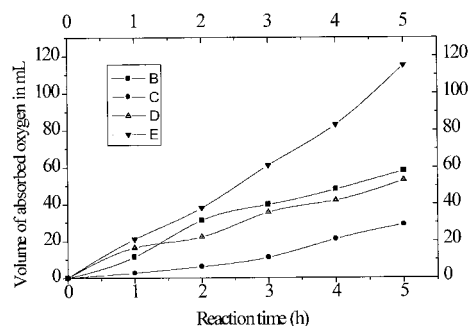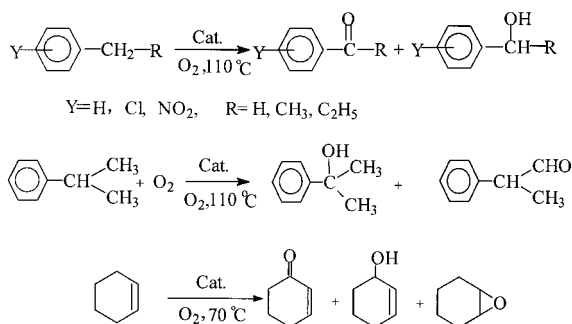
high binding energy (399.5 eV) component has binding energy comparable to what is found for uncoordinated nitrogen (Figure 1, *Eb*, 1s = 399.3 eV). The lower binding energy (*Eb*, 1s = 397.3 eV) component may be belong to the coordinated nitrogen. The result reveals that both free and coordinated bipyridine ligands exist in complex PSBPY-Co. Investigation of the XPS spectra of the complexes PSBPY-CO-bipy, PSBPY-Co-oxine, and PSBPY-Co-phen (Fig. 3) reveals the same result. The decrease of the N(1s) and the increase of $Co(2p_{3/2})$ binding energy indicates that the charge on the nitrogen atoms is increased and that on the cobalt atoms is lowered when polymer-bound cobalt complexes are formed. The change of the charge on both nitrogen and cobalt atoms is due to the electronic donation and antidonation.

Polymer-bound 2,2′-bipyridine cobalt complexes is different from the corresponding iron complexes.[15] The charge on the cobalt atoms in the cobalt complexes is decreased and that on the iron atoms in corresponding iron complexes is increased. In the case of cobalt complexes, the

Table III Effect of Different Catalysts on Reactivity and Product Selectivity[a]

		Selectivity (%)	
Cat.	Ratio (mL/min mol)	1-Phenylethanol	Acetophenone
PSBPY-Co	3.57×10^4	37.1	41.9
PSBPY-Co-bipy	8.91×10^4	34.3	65.2
PSBPY-Co-oxine	5.92×10^4	38.3	61.6
PSBPY-Co-phen	3.83×10^5	36.2	63.7

[a] Reaction conditions: Catalyst 2 mg, ethylbenzene 5 mL, 1 atm of O_2, 5 h at 110°C.

Scheme 2

Figure 8 Catalytic activity of complex (4) (B, after exposure to the air at room temperature for one year; C, newly prepared; D, after exposure to the air at room temperature for one year and reused).

decrease of the charge on the cobalt atoms may suggest that the back donation from cobalt atoms to the π-anti bond orbital of the bipyridine rings exceeds the donation from nitrogen atoms to d orbitals (or hybridized orbitals) of the cobalt atoms.

IR spectra were obtained on an Alpha-Centauri Fourier transform IR spectrophotometer (KBr disks). The IR spectra of the cobalt complexes are shown in Figure 4. The C=N stretching frequencies were shifted to lower region (about 10–30 cm^{-1}) when complexes were formed. This result is in accordance with the XPS analysis. The back donation from cobalt atoms to the π-anti bond orbitals of the bipyridine rings weakens carbon–nitrogen (C=N) bonds and hence results in the C=N stretching frequencies in the IR spectra of the complexes shift to lower values. The suggested structure of the complexes is shown as Scheme 1.
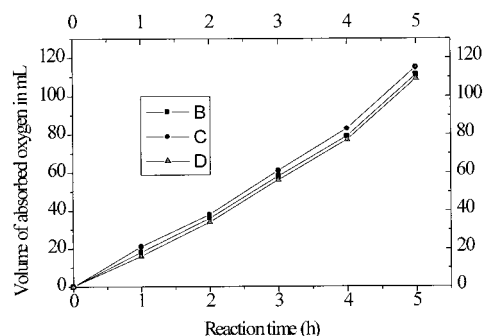
TG-DTA was carried out using a Shimadzu DT-40 thermal analyzer at a heating rate of 15°C min^{-1}. TG-DAT analysis curves for complexes **1–4** revealed weight losses in the temperature range of 216–489, 273–516, 292–473, and 262–520°C, respectively. The corresponding weight loss for complexes **1–4** in above temperature range was 77, 86, 81, and 87%, respectively.

Catalytic Properties

When ethylbenzene is oxidized by molecular oxygen in the presence of polymer-bound cobalt complexes at 110°C, phenylethanol and acetophenone are formed with the molecular oxygen absorption rate of 3.57×10^4 to 3.83×10^5 mL min^{-1} mol^{-1}

Table IV   Oxidation Data of Alkylbenzenes and Cyclohexene Catalyzed by Cobalt Complexes[a]

Substrates	Ratio (mL/min mol)	Product	Selectivity (%)
Toluene	Trace		
p-Xylene	Trace		
o-Nitrotoluene	Trace		
p-Chlorotoluene	Trace		
Ethylbenzene	3.83×10^5	Phenylethanol	36.2
		Acetophenone	63.7
n-Propylbenzen	4.50×10^5	1-Phenylpropanol	24.1
		Ethylphenyl ketone	75.3
Cumene	7.36×10^5	Dimethylphenylmethanol	32.5
		Methylphenylacetaldehyde	67.6
Cyclohexene	1.64×10^5	2-Cyclohexen-1-ol	53.5
		2-Cyclohexen-1-one	24.6

[a] Catalyst, PSBPY-Co-phen (for alkylbenzenes) or PSBPY-Co (for cyclohexene) 2.0 mg, substrate 5 mL, atmospheric pressure of molecular oxygen, 5 h at 110°C (for alkylbenzenes) or 70°C (for cyclohexene).

and the selectivity to total ketone and alcohol of 78% to about 100%. PSBPY-Co, PSBPY-Co-bipy, PSBPY-Co-oxine, and PSBPY-Co-phen are all used as catalysts in this oxidation system. The results are shown in Figure 5, Figure 7, Table III, and Scheme 2; all of the cobalt complexes studied catalyzed the oxidation of ethylbenzene in the given reaction condition. Comparison of the relative efficiencies of catalysts PSBPY-Co, PSBPY-Co-bipy, PSBPY-Co-oxine, and PSBPY-Co-phen in the oxidation of ethylbenzene was carried out. The result showed that complex PSBPY-Co-phen is the most efficient catalyst for the formation of phenylthanol and acetophenone.

Using PSBPY-Co-phen and PSBPY-Co as catalysts, the oxidation of other substrates catalyzed by cobalt complexes was also carried out; the results are shown in Table IV. The oxidation of n-propylbenzene was carried out in the similar reaction condition giving ethylphenyl ketone and 1-phenyl propanol. The oxidation rate of n-propylbenzene is slightly higher than that of ethylbenzene. Cumene was also oxidized in this oxidation process, and affords dimethyl phenyl methanol and methyl phenyl acetaldehyde with the selectivity to total alcohol and aldehyde of 100%. The result is different from that of the oxidation reported in the literature.[19,20] The oxidation of toluene, p-xylene, o-nitrotoluene, and p-chlorotoluene catalyzed by complex **4** gives only trace product.

The oxidation of cyclohexene was performed under 1 atm of molecular oxygen in the presence of polymer-bound cobalt complex PSBPY-Co in the absence of solvent at 70°C, affording 2-cyclohexen-1-ol and 2-cyclohexen-1-one with the conversion of 60% and the selectivity to total alcohol and ketone of 78%.

The catalysts are stable in the air and can be reused. As shown in Figure 8, when complex **4** was reused or was used after exposure to the air at room temperature for one year, the reactivity is slightly lowered.

Conclusion

Polymer-bound cobalt complexes PSBPY-Co, PSBPY-Co-bipy, PSBPY-Co-oxine, and PSBPY-Co-phen were synthesized and investigated by XPS, IR, ICP, TG-DTA, and routine elemental analysis. Both coordinated and free ligands exist in the polymer-bound cobalt complexes.

With the reaction rate of 3.57×10^4 to 3.83×10^5 mL min^{-1} mol^{-1} and selectivity to total ketone and alcohol ranging from 79% to about 100%, the complexes exhibited promising catalytic activity and selectivity for the oxidation of alkylbenzenes and cyclohexene. They are stable in air, convenient for ready separation, and can be reused. They may be used as a viable alternative to environmental hazardous metal-oxide based reagents.

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