Preparation of Polymer-Supported Schiff Base Iron (III) Complexes and Their Catalytic Activity for Decomposition of Hydrogen Peroxide

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SYNOPSIS

Polymeric substrates containing salicylidenimine ligands as discrete units can be obtained by reacting chloromethylated divinylbenzene styrene copolymer with amines, followed by condensation with salicylaldehyde. Polymer-supported Schiff base iron (III) complexes have been prepared and their IR spectra and Mössbauer spectra measured. Catalytic activity of supported complexes have been tested using decomposition of hydrogen peroxide as a model reaction.

INTRODUCTION

Polymer-supported complexes have found numerous applications recently as catalysts in organic synthesis as well as in model reactions.[1-3] Some polymer-supported chelating agents which utilize a Schiff base linkage containing the salicylidenimine ligand have been reported.[4] Drago et al.[5] reported the synthesis and catalytic oxidizing potential of polymer-supported chelating amine and Schiff base complexes.

The decomposition of H_2O_2 catalyzed by iron (III) complexes has received much attention. This is mainly stimulated by the natural occurrence of heme–iron enzyme, i.e., catalase, which enhances the decomposition dramatically.[6] By supporting a complex it is sometimes possible to stabilize catalytically active but normally unstable structures. Recently, Gokak et al.[3] reported the catalytic activity of polymer supported ethylenediamine and glycine cobalt complexes for two model reactions, the hydrogenation of 1-octene and the decomposition of hydrogen peroxide.

We report herein the synthesis and characterization of polymer supported Schiff base iron (III) complexes and their catalytic activity for the decomposition of hydrogen peroxide. The supported Schiff bases contain the following salicylidenenimines:

P—ensal

P—diensal
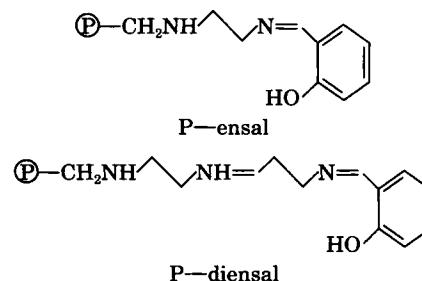
EXPERIMENTAL

Materials and Instrumentation

The chloromethylated divinylbezene styrene copolymer (7% crosslinked) beads were produced by Changjiang Chemical Plant. The other reagents used were of analytical grade.

Infrared spectra were recorded with the Nicolet FT-170SX spectrometer using the KBr pellet technique. Mössbauer spectra were measured with an Elscint Mössbauer spectrometer. The ^{57}Co(Rh-matrix) source had an intensity of around 10 mCi. The isomer shifts are reported relative to $Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$ (SNP). The catalysts

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were analyzed for iron by atomic absorption spectrophotometry.

Preparation of Polymer-Supported Schiff Bases

Chloromethylated polymer beads were swelled in dimethylformamide (DMF) at room temperature for 48 h and then transferred into a three-necked 500 ml round-bottomed flask fitted with a condenser, mechanical stirrer, and addition funnel, and to which 250 mL of ethanol was added. Excess ethylenediamine (en) dissolved in ethanol was added dropwise into the vessel. The reaction mixture was stirred for 20 min at room temperature, and was then warmed to 45°C and kept at this temperature for 24 h with constant stirring. The beads were filtered, and washed with deionized water and ethanol to give P—en. To P—en in a sufficient amount of ethanol to form a slurry is added a large excess of salicylaldehyde. The slurry was heated to 50°C and was kept at this temperature for 36 h with constant stirring. The resulting beads, P—ensal, were filtered, washed with ethanol, and dried at 55–60°C for 48 h under vacuum. For preparing P—diensal, the same procedure was used as for P—ensal except that dien (diethylenetriamine) was used.

Incorporation of Iron (III) into Polymer-Supported Schiff Bases

An excess of $FeCl_3$ was dissolved in 100 mL of ethanol and this used to slurry 2g P—ensal or P—diensal. After 3 days, the resin was filtered, washed with ethanol, and then dried at 55–60°C under vacuum. Incorporation of iron (III) nitrate was accomplished in the same way, except that $Fe(NO_3)_3 \cdot 9H_2O$ was used.

Decomposition of Hydrogen Peroxide

The decomposition rate of H_2O_2 in the presence of supported complexes was measured at 40°C according to Sasaki et al.[7] The initial concentration of H_2O_2 was 14.8×10^{-2} mol/L and the amount of iron was 5.44×10^{-3} g in a buffer reaction system with a volume of 100 mL. The Fe^{3+}-free polymer beads showed no catalysis.

RESULTS AND DISCUSSION

Spectral Characterization of the Samples

The solid state data for the supported complexes are given in Table I.

Infrared spectroscopy was the primary method used to distinguish the nitrate binding in each of the solid-state forms. The presence of four bands is expected in the 1600–800 cm^{-1} region due to the nitrate group, the typical ranges being as follows[8]: bidentate, $1500 \pm 15, 1235 \pm 25, 1010 \pm 10, 810 \pm 10$ cm^{-1}; unidentate, $1450 \pm 40, 1300 \pm 25, 1000 \pm 15, 810 \pm 15$ cm^{-1}. However, for a free nitrate, a strong band at 1380 cm^{-1} is observed.[9] The IR results show that P—ensalFe(NO_3)$_2$ is a supported complex with two unidentate nitrates, while P—diensalFe(NO_3)$_2$ is a supported complex with two free nitrates.

All of the Mössbauer spectra consisted of two doublets. The differences in isomer shift are not noticeable and these parameters may be indicative of high spin iron (III) complexes. However, the differences in quadrupole splitting are considerable. The quadrupole splitting is dependent on the prin-

Table I   Solid State Data for Supported Fe(III) Complexes

Sample	Fe Content (wt %)	IR Bands of Nitrate (cm)	Mössbauer Spectra Parameters (mm s⁻¹, relative to SNP)		
			δ	Δ	Area (%)
P—ensalFeCl$_2$	7.66	—	0.632	0.525	81.0
			0.633	1.007	19.0
P—ensalFe(NO$_3$)$_2$	1.45	1450, 1316	0.564	0.468	88.3
		1016, 823	0.549	0.973	21.7
P—diensalFeCl$_2$	6.60	—	0.624	0.577	89.0
			0.638	1.007	11.0
P—diensalFe(NO$_3$)$_2$	0.19	1380	0.596	0.329	84.4
			0.525	0.540	15.6

Table II   Catalytic Data at 40°C

Catalyst	pH	Adduct and Adduct/Fe Ratio	$k(L \cdot mol^{-1} \cdot min^{-1})$
P—ensal FeCl$_2$	6.1	—	7.60×10^{-3}
	7.0	—	8.71×10^{-3}
	8.0	—	11.01×10^{-3}
	7.0	Py(1 : 1)	6.50×10^{-3}
	7.0	Py(4 : 1)	4.50×10^{-3}
	7.0	Py(6 : 1)	2.51×10^{-3}
	7.0	Im(1 : 1)	7.25×10^{-3}
	7.0	Im(4 : 1)	5.06×10^{-3}
	7.0	Im(6 : 1)	4.25×10^{-3}
P—diensal FeCl$_2$	6.1	—	6.00×10^{-3}
	7.0	—	6.90×10^{-3}
	8.0	—	8.33×10^{-3}
	7.0	Py(1 : 1)	4.57×10^{-3}
	7.0	Im(1 : 1)	4.93×10^{-3}
P—ensalFe(NO$_3$)$_2$	7.0	—	13.30×10^{-3}
P–diensalFe(NO$_3$)$_2$	7.0	—	16.51×10^{-3}

cipal tensor component of the electric field gradient (EFG) at the Fe nucleus. For high spin Fe (III), five d-electrons are evenly distributed to each d orbital, so that EFG is considered only to be the contribution from the nonspheric distribution of the ligands. This suggests that there are two kinds of supported Schiff base groups with different geo-

metric symmetry, and that the lower one leads to a larger value of quadrupole splitting.

Decomposition of Hydrogen Peroxide

For H$_2$O$_2$ concentrations, linear plots of $1/C$ against time were obtained, indicating that the decompo-
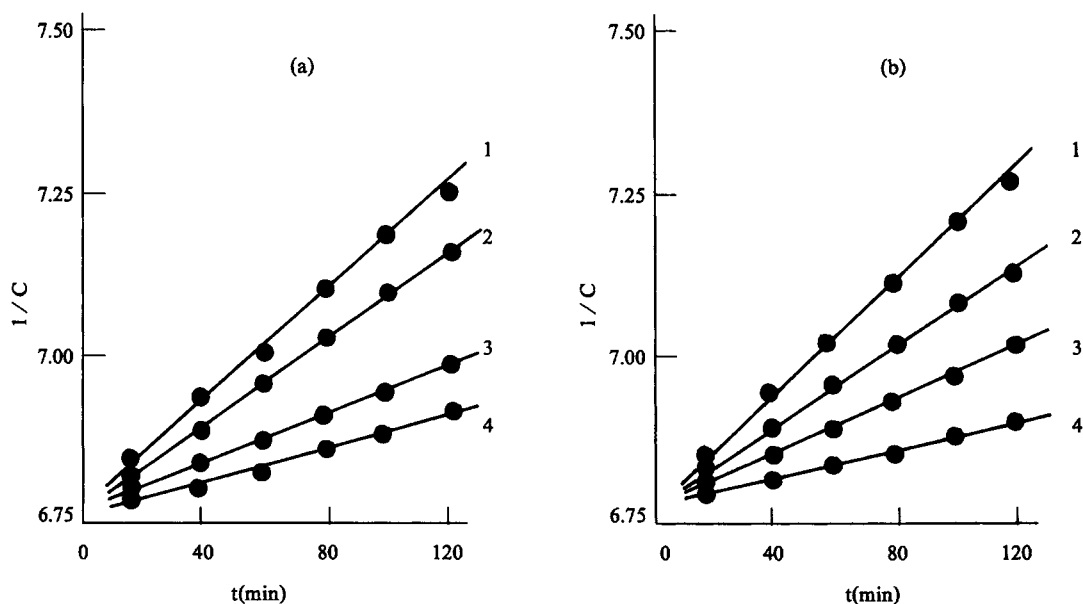

Figure 1   Catalasc-like activity of P—ensal FeCl$_2$ at 30°C. (a) Pyridine/Fe ratio: 1,0; 2,1.0; 3,4.0; 4,6.0. (b) Imidazole/Fe ratio: 1,0; 2,1.0; 3,4.0; 4,6.0.

sition of H_2O_2 catalyzed by the supported complexes is second order in the substrate; the rate constants are listed in Table II. As compared with P—diensalFeCl$_2$, P—ensalFeCl$_2$ has higher catalytic activity, for the reason that the latter provides an additional coordinating site. The catalytic activity of P—diensalFe(NO$_3$)$_2$ is higher than that of P—ensalFe(NO$_3$)$_2$, as indicated above; the former is a supported complex with two free nitrates and therefore the H_2O_2 molecule has easier access to the coordination sphere. Experiments at different pH values have also been carried out and increase in pH increases the rate of reaction in the range of pH 6.1–8.0. As may be clearly seen from Figure 1, adding pyridine (Py) or imidazole (Im) decreases the catalytic activity of the supported complexes and the effect is greater with an increase in the adduct/Fe ratio. The effect can be attributed to the tenacity with which these adducts bind to the iron (III) ion, thus preventing access of H_2O_2 to the coordination sphere.

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