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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Yue Chang^{ab}; Yunpu Wang^a; Fei Zha^a

^a Institute of Chemistry, Northwest Normal University, Lanzhou, P.R. China ^b Department of Chemistry, Lanzhou University, Lanzhou, P.R. China

Online publication date: 22 July 2003

To cite this Article Chang, Yue , Wang, Yunpu and Zha, Fei(2003) 'Preparation and Catalytic Activity of Polymer-Supported 2,4-Dihydroxybenzaldehyde-*o*-aminobenzoic Acid Complexes', *Journal of Macromolecular Science, Part A*, 40: 9, 889 – 896

To link to this Article: DOI: 10.1081/MA-120023525

URL: <http://dx.doi.org/10.1081/MA-120023525>

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JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. A40, No. 9, pp. 889–896, 2003

Preparation and Catalytic Activity of Polymer-Supported 2,4-Dihydroxybenzaldehyde-*o*-aminobenzoic Acid Complexes

Yue Chang,^{1,2,*} Yunpu Wang,¹ and Fei Zha¹

¹Institute of Chemistry, Northwest Normal University, Lanzhou, P.R. China

²Department of Chemistry, Lanzhou University, Lanzhou, P.R. China

ABSTRACT

Polymer-supported 2,4-dihydroxybenzaldehyde-*o*-aminobenzoic acid metal complexes (PS-H₃L-M, M = Cu, Co, Ni, Mn) were prepared and characterized by IR, XPS, and ICP. Their application in the oxidation of cumene with molecular oxygen showed PS-H₃L-Mn having higher catalytic activity. A mechanism for the catalytic oxidation was proposed. The factors influencing the oxidation of cumene by PS-H₃L-Mn were determined, as well the optimal conditions were established.

Key Words: PS-H₃L-Mn; Catalytic oxidation; Cumene.

INTRODUCTION

Transition metal complexes as catalysts for oxidation of hydrocarbons with molecular oxygen have attracted substantial attention in recent years.^[1,2] The reason for this was the growing interest in the studies of the processes of metabolism of harmful organic compounds and production of biologically important materials used in biological systems.

*Correspondence: Yue Chang, Institute of Chemistry, Northwest Normal University, Lanzhou 730070, P.R. China; E-mail: cy70@sina.com.



Among the variety of ligands employed so far, the noteworthy examples include porphyrin derivatives, macrocyclic polyamines, and schiff-base.^[3-5] A number of transition metal ions, viz., Mn(II), Fe(III), Ru(II), Co(II), etc., have been utilized. Although these homogenous catalysts possess higher activity and selectivity, they are not easily separated from reaction mixtures and are allowed for repeated use. These flaws influence practical application. Comparatively, the polymeric approaches to catalyst design have some certain advantages. The polymer-supported catalyst not only retains the activity and selectivity of well-defined homogeneous catalysts, but also offers an efficient means for recovery and recycling of expensive catalysts. For example, metal-complexes of porphyrin and Schiff-base anchored to polymeric supports have been reported to be suitable catalysts in the oxidation of cyclohexane with molecular oxygen.^[6,7] In this paper, we used polymer-supported 2,4-dihydroxybenzaldehyde-*o*-aminobenzoic acid manganese complex as catalyst in the oxidation of cumene without co-reducer. At 373 K, the conversion of cumene was superior to earlier reports.^[8,9]

EXPERIMENTAL

Chemicals

Chloromethylated polystyrene, 2,4-dihydroxybenzaldehyde, *o*-aminobenzoic acid, anhydrous ethanol, acetone, cumene, and metal compounds were obtained commercially. Solvents were distilled before being used.

Apparatus

The metal contents of the supported catalysts were analyzed on a model ARL-3520 Inductively Coupled Plasmas Atomic Emission Spectrometry made in USA. The IR spectra were recorded in KBr on an Alpha-centauri FT-IR spectrophotometer. X-ray photoelectron spectroscopy (small area XPS) data were recorded with the PHI-5702 Multi-Technique System, Power Source by MgK _{α} line and Ag_{3d5/2} FWHM \leq 0.48 eV. The products of oxidation were determined and analyzed by GC-16A Gas Chromatograph and QP-1000A GC/MS system.

Synthesis of 2,4-Dihydroxybenzaldehyde-*o*-aminobenzoic Acid Manganese Complex (H₃L-Mn)

According to a method described in the literature:^[10] 2,4-dihydroxybenzaldehyde (1.96 g, 0.01 mol) was mixed with 40 mL of distilled ethanol solution of manganese acetate (2.45 g, 0.01 mol) in a 100 mL round-bottom flask. The mixture was stirred using a magnetic stirrer at 323–333 K. *o*-Aminobenzoic acid (1.37 g, 0.01 mol) dissolved in 20 mL of ethanol was added dropwise using a dropping funnel to the above solution. The mixtures were stirred for 3 hr to get a pink solid precipitate of H₃L-Mn, which was filtered off and washed with hot ethanol and dried.



Synthesis of PS-H₃L-Mn

The chloromethylated polystyrene (1.4 g) was swelled in acetone for about 12 hr. An acetone solution of H₃L-Mn (3.0 g) was added to the above suspension. The mixture was refluxed for 24 hr, with stirring and then cooled to room temperature. The pink resin was filtered, extracted using a Soxhlet apparatus until the filtrate was colorless, followed by drying under vacuum. Other metal complexes PS-H₃L-M, where M = Cu, Co, and Ni, were prepared by the same method.

Oxidation Procedure

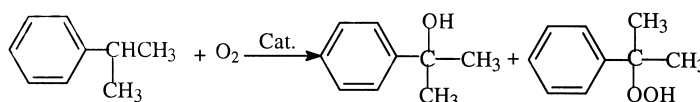
In this paper, the same oxidation reaction as described in Ref.^[4] was carried out. Catalyst and substrate were added in a glass reactor with a gas inlet tube connected to a gas burette and an oxygen storage bottle along with a gas outlet tube that could open to the air. The mixture in the reactor, after repeated purging with oxygen, was stirred with a magnetic stirrer and heated to 353 K. The volume of oxygen consumed was measured from the burette. The reaction products were analyzed on a Shimadzu QP-1000A GC/MS system and a GC-16A model. The main products are cumene hydroperoxide (CHP) and 2-phenyl-2-propanol (PP) (see Sch. 1).

RESULTS AND DISCUSSION

Characterization

IR spectra show a band at 1629 cm⁻¹ attributed to the $\nu_{C=N}$ stretch. In the polymer-supported complex this band undergoes a negative shift of about 5 ~ 17 cm⁻¹, indicating the involvement of the azomethine nitrogen atom in coordination.^[8] The absorption of polymer complexes shown at 1550 and 1410 cm⁻¹ are due to the ν_{asCOO} and ν_{sCOO} , respectively. Compared with the absorption peak at 1245 cm⁻¹ attributed to the phenolic group, a shift of about 1300 ~ 1200 cm⁻¹ is observed, which is indicative of the coordination of the metal ion with the phenolic oxygen atom on the ligand. Two new bands appeared nearby 420 and 350 cm⁻¹ in polymer-supported complexes, due to the absorption of M—O and M—N, respectively.^[9]

In order to prove the coordination of polymer-supported complexes, small area XPS data of polymer ligand and its complex have been studied (Table 1). Compared with manganese acetate, the binding energy of Mn_{2p3/2} increases 0.96 eV. The change of the Mn_{2p3/2} binding energy means a decrease of its electron density. On the other hand, the N_{1s1/2} binding energy of polymer complex decreases 0.6 eV, compared to the



Scheme 1. Oxidation reaction of cumene.



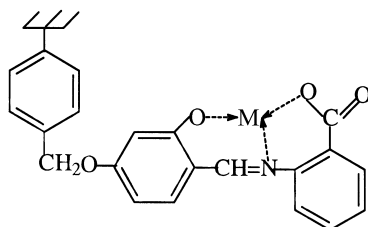
Table 1. X-ray photoelectron spectroscopy data of different substances.

Substance	XPS peak	Bind energy (eV)	ΔE_b (eV)
Mn(OAc) ₂	Mn _{2p_{3/2}}	640.6	0.0
H ₃ L	O _{1s_{1/2}}	531.9	0.0
	N _{1s_{1/2}}	400.0	0.0
H ₃ L-Mn	Mn _{2p_{3/2}}	641.56	+0.96
	O _{1s_{1/2}}	531.5	-0.4
	N _{1s_{1/2}}	399.5	-0.5
PS-H ₃ L-Mn	Mn _{2p_{3/2}}	641.2	-0.36
	O _{1s_{1/2}}	531.6	-0.1
	N _{1s_{1/2}}	399.6	+0.1

corresponding low molecular ligand (H₃L). The electronic states of the nitrogen and oxygen atom in the polymer complex are of higher electron density and, therefore, the electrons in the manganese atom may flow into the nitrogen atom to form a N–Mn coordination bond. The oxygen peak in the complex could be divided into three peaks attributable to oxygen atoms in the phenolic and carbonyl groups. The O_{1s_{1/2}} binding energy of the polymer complex is lower than that of the corresponding support. According to analysis, this change indicates that oxygen atom in the –O*H and –COO*H groups bind to the metal ion. The proposed structure of the complex is shown in Sch. 2.

Effect of Metal Ions

The kinetic curves for different investigated catalysts are shown in Fig. 1. It is clear that the reaction has a shorter induction period for PS-H₃L-Co, PS-H₃L-Ni, and PS-H₃L-Mn, respectively, while PS-H₃L-Cu has a larger one. With the extending of reaction time, the consumption of oxygen continuously increases. When the reaction was carried out for about 7 hr, the amount of consumed oxygen by the metal catalysts follow the order of Cu > Mn > Ni > Co. However, the conversion of cumene indicates that the activity of Mn catalyst is higher than that of Cu (Table 2). In addition, the PS-H₃L-Mn catalyst possesses the biggest turnover number among the above catalysts at 363 K, which is given by content of metal per gram of catalyst and the consumption of oxygen in cumene (1 mL). According to the phenomenon of reaction, the mechanism of the autoxidation of cumene using



Scheme 2. The structure of PS-H₃L-M.

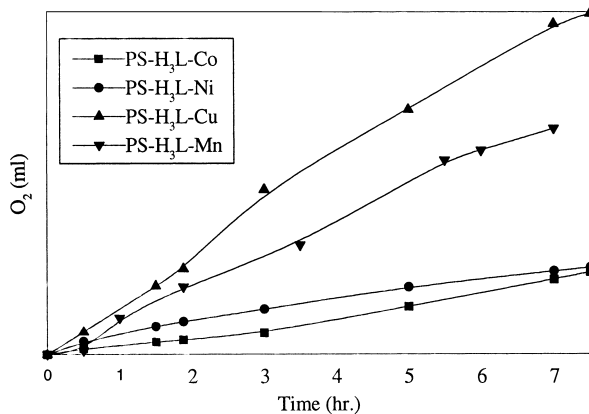


Figure 1. Effect of various metal ions on catalytic oxidation. Catalyst, 2 mg; cumene, 1 mL; temperature, 373 K.

PS-H₃L-M (M: Cu, Co, Ni, Mn) catalyst is different from the reported.^[8,9] The following mechanism is proposed:



In this mechanism, the metal ions function both as an initiator and as a catalyst of hydroperoxide decomposition. As seen in Fig. 2, in the first hour, the content of cumene

Table 2. Oxidation of cumene in the presence of various catalysts.

Catalyst	Metal (%)	Conversion (%)	Selectivity (%)		Turnover number (mol/mol hr)
			CHP	PP	
PS-H ₃ L-Co	2.9	21.1	62.1	23.8	18,990
PS-H ₃ L-Ni	8.8	10	60.0	25.1	6,570
PS-H ₃ L-Cu	7.3	40.2	40.4	53.1	25,770
PS-H ₃ L-Mn	2.4	59.1	46.0	44.7	28,857

Note: Temperature, 363 K; catalyst, 2 mg; cumene, 1 mL; reaction time, 7 h.



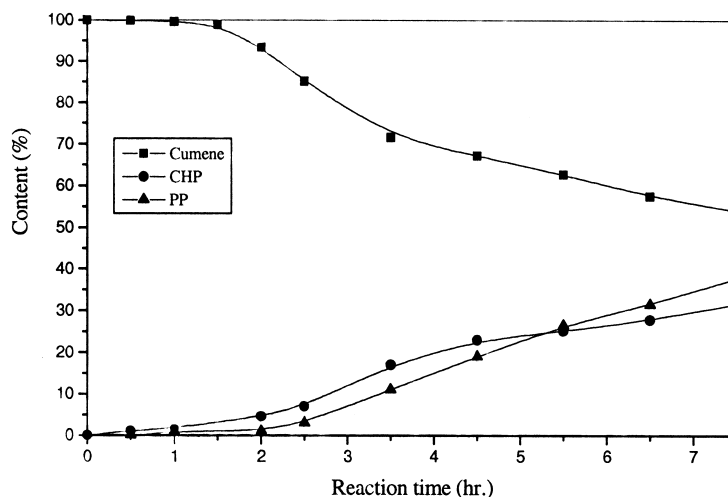


Figure 2. Relationship between the content of every component with reaction time in oxidation system.

almost does not change. With the passage of time, the content of cumene decreases, meanwhile, the content of CHP and PP increase. In addition, after the reaction has been carried out for 5 hr, the rate of production of PP is faster than that of CHP.

Effect of Temperature

The catalytic activity of PS-H₃L-Mn was investigated as a function of temperature. The conversion of cumene and the selectivity of products in a reaction mixture of 1 mL of cumene with 2 mg of PS-H₃L-Mn at 353, 363, 373, and 383K are collected in Table 3. The results indicate that increasing the reaction temperature is advantageous for generating PP. However, the selectivity of CHP drops from 49.9% to 39.9%. More importantly, the conversion of cumene is higher at 373K than that of previously reported.^[8,9]

Table 3. Product distribution of cumene at various temperatures.

Temperature (K)	Conversion (%)	Selectivity (%)	
		CHP	PP
353	46.3	49.9	33.9
363	59.1	46.0	44.7
373	79.6	40.6	49.0
383	62.5	39.9	55.0

Note: Catalyst, 2 mg; cumene, 1 mL; reaction time, 7 h.



Table 4. Product distribution of oxidation of cumene in various amounts of PS-H₃L-Mn.

Catalyst (mg)	Conversion (%)	Selectivity (%)	
		CHP	PP
0.5	26.9	50.6	39.1
1.0	30.6	66.0	30.3
3.0	57.7	73.8	23.9
5.0	19.7	74.7	18.0

Note: Temperature, 373 K; cumene, 3 mL; reaction time, 7 h.

Effect of the Amount of Catalyst

At 373 K, the results of oxidation of cumene in the presence of various amount of PS-H₃L-Mn are shown in Table 4. When the concentration of cumene is fixed, and the amount of catalyst is increased from 0.5 to 3.0 mg, the conversion of cumene raises from 26.9% to 57.7%. It decreases from 57.7% to 19.7% when the amount of catalyst increases from 3.0 to 5.0 mg. The results indicate that there is an optimal amount of catalyst that should be used and that an increasing amount of catalyst does not improve the conversion of cumene. However, for the selectivity of the products, with the increasing of amount of catalyst, the selectivity of CHP increases, while that of PP decreases.

CONCLUSION

The polymer-supported 2,4-dihydroxybenzaldehyde-*o*-aminobenzoic acid manganese complex is the most effective catalyst for the oxidation of cumene by molecular oxygen in these catalysts (PS-H₃L-M, M = Cu, Co, Ni, Mn). The major products are PP and CHP. This catalyst possesses the following desirable properties: (1) the optimum temperature is at 373K and the conversion is higher than literature reports^[9,10] and (2) increasing the amount of catalyst is advantageous for generating CHP.

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Received December 2002

Revised January 2003

