

Oxidation of Styrene over Polymer- and Nonpolymer-Anchored Cu(II) and Mn(II) Complex Catalysts

Sweta Sharma,¹ Shishir Sinha,¹ Prakash Biswas,¹ Mannar R. Maurya,² Shri Chand¹

¹Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee 247667, Uttarakhand, India

²Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, Uttarakhand, India

Correspondence to: S. Sinha (E-mail: shishir@iitr.ernet.in)

ABSTRACT: Catalytic oxidation of styrene was investigated over polymer- and nonpolymer-anchored Cu(II) and Mn(II) complex catalysts prepared by schiff base tridentate ligands. The effect of temperature, styrene to H₂O₂ mole ratio and catalyst amount on the catalytic activity and product selectivity was investigated. Further, the catalysts were characterized by various techniques, such as elemental analysis, atomic absorption spectroscopy (AAS), FTIR, FE-SEM, EDAX, TGA, and UV-vis spectrophotometer. The elemental analysis, EDAX and AAS results confirmed the formation of Cu(II) and Mn(II) complexes, and it was found that the metal loading in the polymer-anchored complex catalysts were in the range of 0.53–3.74 %. FTIR results showed the co-ordination bond formation between the polymer ligands and metal ion. The catalytic data showed that, over all the catalysts, the main reaction products were benzaldehyde, styrene oxide, and benzoic acid. The polymer-anchored complex catalysts were found to be much more active when compared with nonpolymer-anchored catalysts. The maximum conversion of styrene (92.3%) was obtained over PS-[Cu(Hfsal-aepy)Cl] catalyst with benzaldehyde selectivity to 69% at the styrene to H₂O₂ mole ratio of 1 : 4 at 75°C. Although the PS-[Mn(Hfsal-aepy)Cl] catalyst was less active, it was highly selective to benzaldehyde. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Catalytic oxidation of alkenes is an important reaction usually used in the catalytic synthesis of organics in industries. The resultant epoxides are used in the manufacture of a wide range of fine chemicals such as phenethyl alcohol, phenylaldehyde, perfume, and drugs. Traditionally, liquid-phase oxidation of alkenes is carried out by using stoichiometric amounts of organic peracids such as peracetic acid and *m*-chlorobenzoic acid with permanganate as the oxidizing agent.¹ However, peracids are very expensive, hazardous, and nonselective to epoxide and also propagate the formation of undesirable side products, which create environmental pollution. In last few years, much attention has been paid for the oxidation of alkenes in the presence of various environment friendly oxidants such as hydrogen peroxide, *tert*-butyl hydroperoxide (TBHP), and oxygen.^{2–6} Hydrogen peroxide is an attractive oxidant as it is cheap, mild, and gives water as the only by-product. From the industrial point of view, liquid-phase oxidation of styrene is of great importance. The main products obtained by the oxidation of styrene are styrene oxide and benzaldehyde. These are major valuable organic

intermediates for the production of fine chemicals. Various complexes of transition metals have been tested for the catalytic oxidation of styrene. Design of effective catalysts is crucial and some promising catalysts have been used for styrene oxidation reaction. Rayati et al.⁷ studied the oxidation of cyclooctene and styrene using oxovanadium (IV) schiff base catalyst and reported higher activity (92%) for the conversion of cyclooctene to cyclooctene oxide. They also found that oxovanadium (IV) Schiff base catalyst was less active for styrene oxidation. Choudhary and coworkers⁸ investigated the oxidation of styrene over Al₂O₃-, Ga₃O₃-, In₂O₃-, and Tl₂O₃-supported Au catalyst, and found maximum activity and selectivity to styrene oxide on Tl₂O₃-supported Au catalyst. Han and coworkers⁹ synthesized nickel containing ionic liquid immobilized on silica and tested for the oxidation of styrene at solvent-free conditions. They reported 96% selectivity to benzaldehyde over nickel-based catalyst. The oxidation of styrene over copper-based catalysts tested by Xiao and coworkers¹⁰ and showed that copper catalyst was active for oxidation of styrene with 60% selectivity to benzaldehyde. Yuan and coworkers¹¹ have shown that, under mild

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reaction condition, over TBHP, copper-containing hexagonal mesoporous silica was highly active and selective for the oxidation of styrene to styrene oxide. Pierella and coworkers¹² studied the styrene oxidation using Cu(II), Zn(II), Mn(II), Cr(II), Co(II), and Fe(II) supported on zeolite and found the highest selectivity to benzaldehyde (78.0%) over Cr(II) catalyst using H₂O₂ as oxidant.

Recently, the use of polymer-supported catalysts in organic transformations has received a considerable attention because polymer supports are nonreactive, insoluble, offers wide range of surface area for tailor made applications, allows easy incorporation of catalyst into polymer structure, and produces less solid waste compared to metal-supported catalyst, which makes overall process more economical and environmental friendly.¹³ Gupta et al.¹⁴ reviewed polymer-anchored schiff base complexes as catalyst for the oxidation of alkenes and reported that various transition metal catalysts were very promising. Polymer-supported metal complexes, especially with schiff bases, has shown considerably high activity and selectivity for the oxidation of various olefins and alcohols under various reaction conditions.^{15–17} Sherrington et al.^{18–20} designed and synthesized various polymer supports by the immobilization of Mo(VI) metal and tested for epoxidation of alkene in presence of *tert*-butylhydroperoxide. Tembe and coworkers^{21–23} investigated the catalytic epoxidation of styrene, cyclohexane, and cyclooctene on schiff base Ru(III) metal complexes anchored on chloromethylated styrene–divinylbenzene resin. The catalysts were recycled four times; however, low selectivity (14.7%) to styrene oxide has been reported over Ru(III) metal complex. Chang et al.²⁴ reported higher activity of polystyrene-supported schiff base metal complexes catalyst for the oxidation of cyclohexene in the presence of molecular oxygen of different transition metal complexes. The Cu(II)-based catalyst showed highest catalytic activity (52%) among various metal complexes tested.

In this study, liquid-phase oxidation of styrene with its product distribution has been studied over polymer- and nonpolymer-anchored Cu(II) and Mn(II) complex catalysts. The effect of temperature, styrene to H₂O₂ mole ratio, and catalyst amount on styrene oxidation has been investigated. The activities of polymer-anchored catalysts were compared with nonpolymer-anchored catalysts. The recyclability of all the polymer-anchored catalysts was also evaluated.

EXPERIMENTAL

Synthesis of Catalyst

Chloromethylated polystyrene (18.9% Cl, i.e., 5.3 mmol Cl per gram of the resin and cross-linked with 5% divinylbenzene) was obtained from Thermax Limited, Pune, India. 3-Formyl salicylic acid (Hfsal) covalently bounded to chloromethylated polystyrene (PS) cross-linked with 5% divinylbenzene reacted with *N,N*-dimethylethylenediamine (dmen) and 2-(2-aminoethyl)pyridine (aepy) to give the Schiff base tridentate ligands PS-[Hfsal-dmen] and PS-[Hfsal-aepy] (Figure 1). These anchored ligands reacted with CuCl₂·2H₂O and MnCl₂·4H₂O to form the complexes PS-[Cu(Hfsal-dmen)Cl], PS-[Cu(Hfsal-aepy)Cl], PS-[Mn(Hfsal-dmen)Cl] and PS-[Mn(Hfsal-aepy)Cl].²⁵ The nonpolymer-anchored complexes (sal-dmen) and (sal-aepy) were

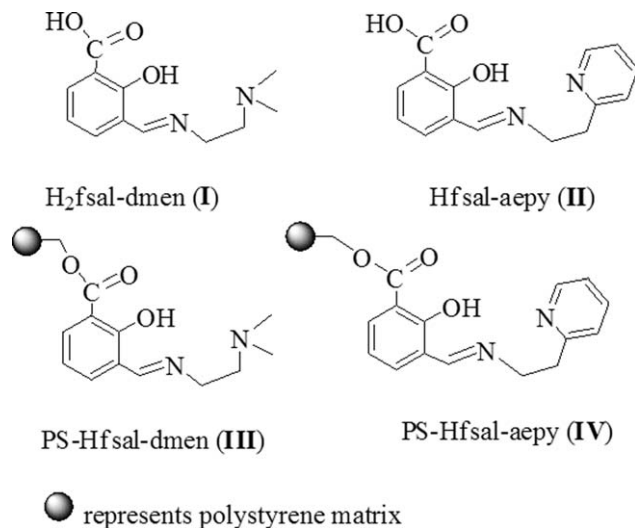


Figure 1. Structure of polymer anchored ligands.

synthesized according to the procedures reported by Mitra and coworkers²⁶ and Tandon et al.²⁷ The synthesis procedure of the nonpolymer- and polymer-anchored complex catalysts are described below.

Synthesis of Nonpolymer-Anchored Catalysts

[Cu(sal-aepy)Cl] (C-1). Salicylaldehyde (0.61 g, 5 mmol) was added to 10 ml methanol. A solution of 2-(2-aminoethyl) pyridine (0.61 g, 5 mmol) in 10 ml methanol was prepared separately. The methanolic solution of salicylaldehyde was then added to the 2-(2-aminoethyl) pyridine-methanol solution dropwise with stirring at room temperature, and the resulting mixture was then refluxed for 1 h at room temperature. A solution of CuCl₂·2H₂O (0.85 g, 5 mmol) in methanol (10 ml) was prepared in a separate beaker, and this Cu-solution was then added dropwise to the previous reaction mixture. The resulting solution was then stirred vigorously for 4 h. The final liquid mixture obtained was then kept in refrigerator overnight. The resulting black solid obtained was filtered, washed thoroughly with methanol, and dried in a vacuum oven at 80°C.

[Mn(sal-aepy)Cl] (C-2), [Cu(sal-dmen)Cl] (C-3), and [Mn(sal-dmen)Cl] (C-4). These complexes were synthesized following the same procedure as mentioned for [Cu(sal-dmen)Cl] complex. For these complexes, sal-aepy (5 mmol) was synthesized in situ and respective metal chlorides (5 mmol) salts were used as catalysts precursors.

Synthesis of Polymer-Anchored Catalysts

PS-[Cu(Hfsal-aepy)Cl] (Cu-A). The polymer-anchored ligand PS-[Hfsal-aepy] (2.0 g) was allowed to swell in 30 ml methanol for 30 min. A solution containing 3.75 g (22 mmol) of CuCl₂·2H₂O (99.0%, S.D Fine Chemicals, India) in 30 ml methanol was prepared separately. The copper salt solution was then added to the solution containing PS-[Hfsal-aepy] dropwise, and the resulting mixture was heated at 60°C in a thermostated oil bath with reflux for 18 h with continuous stirring. The liquid mixture was then cooled down to room temperature. The resin

Table I. Physical and Analytical Data of Polymer-Anchored Ligand, Polymer-Anchored Metal Complexes, and Nonpolymer-Anchored Complexes

Compound	Catalyst	Color	Elements (%) ^a			Metal loading (wt %)	S _{BET} (m ² /g)
			C	H	N		
PS-[Hfsal-dmen]	L-1	Orange	68.6	8.1	3.8	—	18.54
PS-[Hfsal-aepy]	L-2	Dark orange	71.7	5.8	4.4	—	20.45
PS-[Cu(Hfsal-aepy)Cl]	Cu-A	Black	56.2	5.6	1.8	1.97	16.47
PS-[Cu(Hfsal-dmen)Cl]	Cu-B	Brown	65.3	8.1	2.3	3.74	14.21
PS-[Mn(Hfsal-aepy)Cl]	Mn-A	Maroon	59.8	4.0	1.9	1.24	15.68
PS-[Mn(Hfsal-dmen)Cl]	Mn-B	Red	65.8	5.6	2.2	0.53	16.73
[Cu(sal-aepy)Cl]	C-1	Dark green	53.8 (54.0)	4.3 (4.7)	8.4 (8.8)	—	—
[Mn(sal-aepy)Cl]	C-2	Black	36.9 (36.6)	2.2 (3.7)	7.8 (8.1)	—	—
[Cu(sal-dmen)Cl]	C-3	Yellow	52.8 (53.2)	3.6 (4.0)	8.5 (8.8)	—	—
[Mn(sal-dmen)Cl]	C-4	Green	51.6 (51.8)	3.7 (4.0)	8.4 (8.6)	—	—

^aValues within parens indicate theoretical values for nonpolymer-anchored complexes.

was then filtered, washed thoroughly with hot methanol (60°C), and dried at 80°C in oven.

PS-[Mn(Hfsal-aepy)Cl] (Mn-A). The PS-[Mn(Hfsal-aepy)Cl] complex was synthesized following the same procedure as discussed for the synthesis of PS-[Cu(Hfsal-aepy)Cl] complex. PS-[Hfsal-aepy] and MnCl₂·4H₂O (99.0%, SD Fine Chemicals, India) were used as the catalyst precursor.

PS-[Cu(Hfsal-dmen)Cl] (Cu-B) and PS-[Mn(Hfsal-dmen)Cl] (Mn-B). The PS-[Cu(Hfsal-dmen)Cl] and PS-[Mn(Hfsal-dmen)Cl] complexes were also prepared following the same method. PS-[Hfsal-dmen] was used as ligand and CuCl₂·2H₂O (3.75g, 22mmol), and MnCl₂·4H₂O (4.34 g, 22 mmol) salts were used as metal precursors for Cu- and Mn-complexes.

Characterization of Catalysts

Elemental analysis of the ligands and complexes were determined by an Elementar model Vario-EL-III, USA. Metal content in the polymer-anchored complexes were estimated by atomic absorption spectroscopy (AAS) (GBC Avanta atomic absorption spectrophotometer, Australia). Typically, 0.1 g of the catalyst sample was digested with 10 ml concentrated HNO₃. The obtained solution was then diluted to 50 ml in a volumetric flask by distilled water and was analyzed by AAS. The BET surface area was determined by N₂ adsorption/desorption isotherms at 77 K, using ASAP 2020 (Micromeritics, USA). FTIR was performed to identify the interactions of the transition metals with the functional groups present on polymer supports as well as other coordinated ligands. The spectra were recorded from KBr pellets on a Nicolet (NEXUS Aligent 1600, USA) in the range of 4000–400 cm⁻¹. To understand the morphological changes occurred on the surface of polymer anchored complexes, FE-SEM and EDAX analysis of the anchored ligands as well as complexes were recorded by FEI Quanta 200 FEG, USA. To determine the thermal stability of the complex catalysts, TGA were performed in Perkin Elmer (Pyris Diamond, USA) equipment with an accuracy of 1 μg. For each run, 10 mg catalyst was analyzed in the temperature range of 25–750°C, at a temperature ramp of 10°C min⁻¹. Electronic spectra of the

polymer-bound complexes were recorded in Nujol on a UV-vis spectrophotometer (Shimadzu 1601, Japan). To record the spectra of nonpolymer bound complexes, methanol was used as a solvent.

Catalyst Testing

Catalytic oxidation of styrene was carried out in a 50-ml, two-neck flasks equipped with reflux water condenser. The whole assembly was placed on a temperature controlled oil bath. In a typical reaction procedure, the catalyst (25 mg) was allowed to swell in 10 ml acetonitrile for 30 min. Styrene (1.04 g, 10 mmol) was added to this reaction mixture followed by the addition of 30% H₂O₂ (2.28 g, 20 mmol). The reaction mixture was heated at 80°C for 6 h with continuous stirring. The products samples were collected at every half-an-hour time interval for analysis.

The products were analyzed by gas chromatography (GC; Thermo Scientific, USA). The GC, equipped with a capillary column of length 30 m, ID 0.25 mm, and film (dimethyl polysiloxane) thickness of 0.25 μm and a flame ionization detector with N₂ as the carrier gas, was used for the separation of benzaldehyde, phenylacetaldehyde, styrene oxide, benzoic acid, and 1-phenylethane-1, 2-diol. The products were also confirmed through gas chromatography-mass spectrometry (Perkin-Elmer Clarus 500, USA). For calculating the selectivity of the products, iso-octane was used as the internal standard. For the reported runs, the carbon balance was 100 ± 5%.

The selectivity of the products and turn over frequency (TOF) is defined as follows:

$$S_X(\%) = (\text{moles of product} / \text{total moles of products}) \times 100.$$

$$\text{TOF} = [\text{moles of substrate converted} / (\text{time [h]} \times \text{moles of metal})]$$

RESULTS AND DISCUSSION

Catalyst Characterization

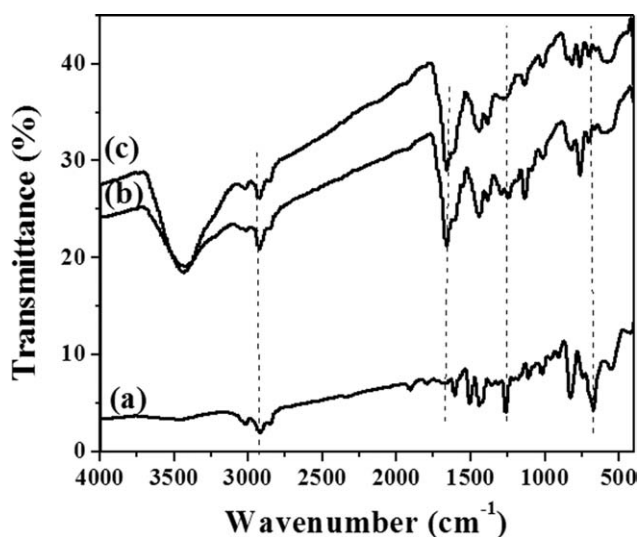
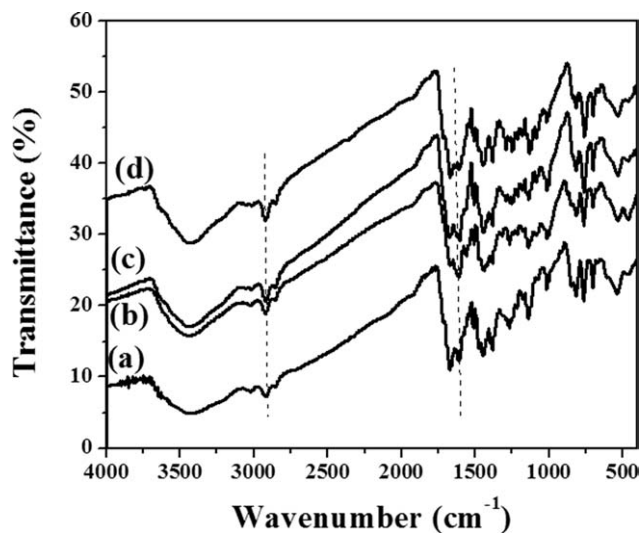
The physicochemical data of the ligands, nonpolymer-anchored, and polymer-anchored complex catalysts were determined by the elemental analysis, and the metal content of the polymer

Table II. Ligand Loading, Metal Loading, and Their Ratios

Catalysts	Ligand loading (mmol g ⁻¹ of resin)	Metal ion loading (mmol g ⁻¹ of resin)	Ligand : metal ratio
Cu-A	0.71	0.57	1.2 : 1
Cu-B	0.64	0.52	1.2 : 1
Mn-A	0.78	0.66	1.2 : 1
Mn-B	0.82	0.67	1.2 : 1

complexes was determined by AAS. The results are shown in Table I. The AAS results confirmed the presence of copper and manganese metal in the complexes formed.²⁸ The metal content of all the polymer-anchored metal complexes were very low and it was in the range of 0.53–3.74 wt %. The low content of metal in the complexes may be due to the limited availability of reactive functionalities.^{29–31} Table I showed the surface area (S_{BET}) of ligands and polymer-anchored complexes and showed decrease in surface area when metal was anchored onto the support. The ligand loading, metal loading, and their ratios were calculated using the method reported earlier.³² The ligand loading were in the range of 0.64–0.82 mmol g⁻¹ of resin whereas metal ion loading was in the range of 0.52–0.67 mmol g⁻¹ of resin as shown in Table II. The ligand to metal ratio for the catalysts Cu-A, Cu-B, Mn-A, and Mn-B were 1.2 : 1.

The FTIR spectra of chloromethylated polystyrene bead polymer ligands and metal complexes are shown in Figures 2 and 3, respectively. The FTIR spectra of chloromethylated polystyrene showed two strong peaks at the wavenumber of 673 and 1264 cm⁻¹ (Figure 2A). These peaks corresponded to C-Cl bond.³³ For the polymer-anchored ligands L-1 (Figure 2B) and L-2 (Figure 2C), these peaks were absent, which indicated that there was no C-Cl bonding. The chloromethylated polystyrene may be bonded covalently with L-1 and L-2 ligands. The polymer-anchored ligands exhibited a sharp band at 1670 cm⁻¹ due to

**Figure 2.** FTIR spectrum of (A) pure polystyrene bead, (B) ligand L-1, and (C) ligand L-2.**Figure 3.** FTIR spectrum of (A) Cu-A, (B) Mn-A, (C) Cu-B, and (D) Mn-B.

the $\nu(\text{C}=\text{O})$ (Figure 2B,C). Existence of this band suggested the covalent bond formation between the ligands and the polymer occurred through an ester group.³⁴ A strong band at the wave number of 1630 cm⁻¹ was also detected for the polymer-anchored ligands due to the presence of azomethine group ($\text{C}=\text{N}$). In polymer-anchored complexes (Figure 3A–D), the band corresponding to $\text{C}=\text{N}$ was shifted to lower wavenumber (1629, 1613, 1618, and 1620 cm⁻¹), which suggested the formation of coordination bond between azomethine nitrogen and metal ion.³⁵ Similar kind of coordination bond formation through coordinating atoms of monobasic tridentate ligands via ($\text{O}-\text{N}-\text{N}$) functionalities have been reported by Maurya et al.²⁵ in oxovanadium (IV and V) complexes. The band obtained at the medium intensity covering the range of 2700–2900 cm⁻¹ in all spectra was corresponded to $[-\text{CH}_2]$ groups. The FTIR spectra of nonpolymer-anchored metal complexes were very close to the FTIR spectrum of polymer-anchored analogs (data not shown).^{36,37}

The FE-SEM micrograph and the EDAX data obtained for polymer-anchored ligands and metal complexes are shown in Figure 4. The EDAX data on the top surface of the ligand showed that the chlorine and nitrogen content was 3 and 7%, respectively, whereas the chlorine content of pure polystyrene bead was 17% (data not shown). The FE-SEM images (Figure 4A–C) of ligand L-1 as well as Cu-A and Mn-A metal complexes showed that the top surface was slightly rough in nature. The formation of rough surface occurred may be due to the strong interaction in between metal ions and ligands during the complex formation. The presence of copper and manganese was confirmed by the EDAX data of complexes, which also confirmed the formation of metal complexes with the ligand (Figure 4B,C).

The stability of the polymer-anchored complexes was investigated by TGA analysis in the temperature range of 100–750°C, as shown in the Table III. The TGA data showed that the polymer-anchored complex catalysts (Cu-A, Cu-B, Mn-A, and Mn-B) were decomposed mainly in three major steps. The first step

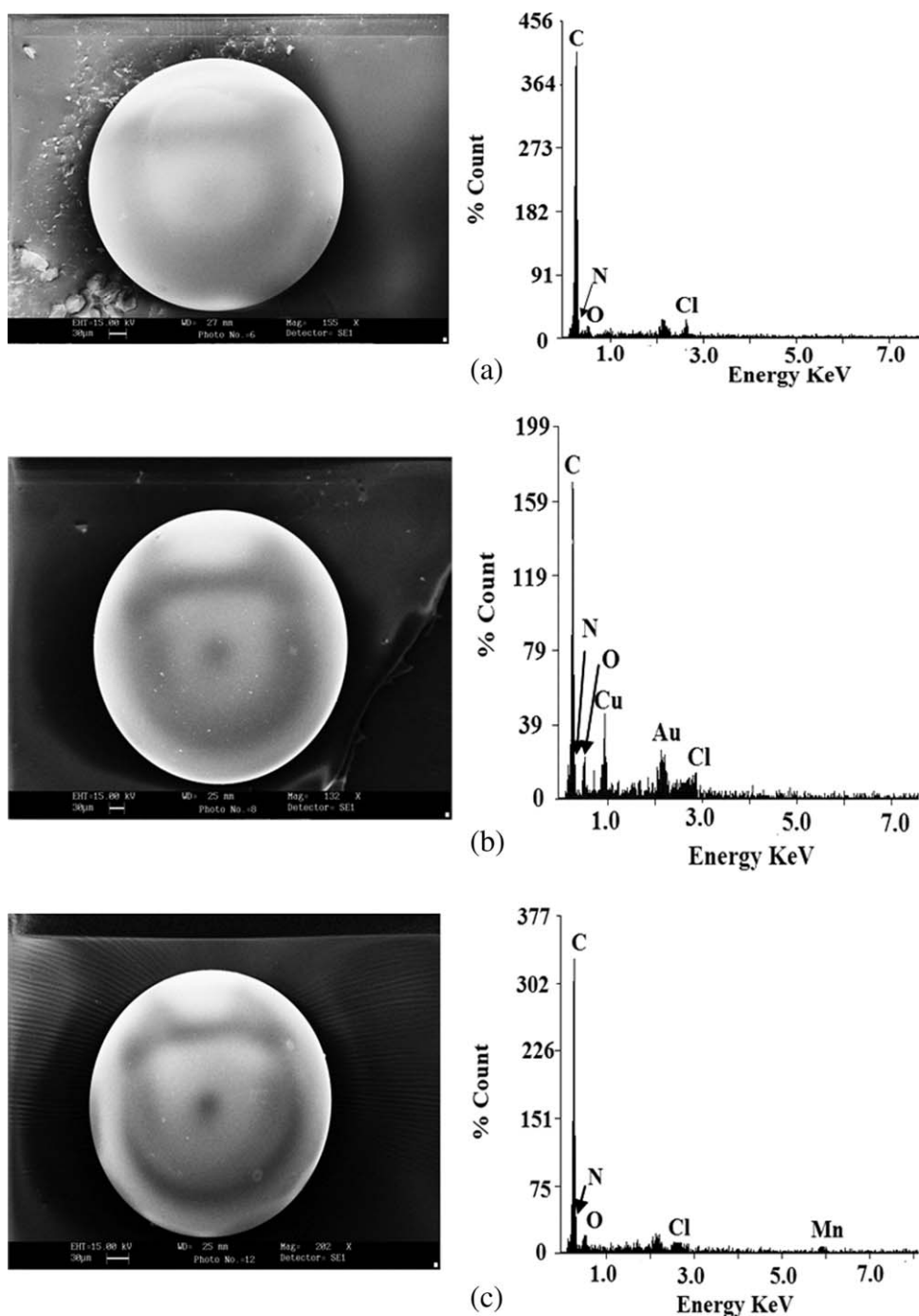


Figure 4. EDAX profiles of (A) L-1, (B) Cu-A, and (C) Mn-A.

of weight loss was in the temperature range of 80–200°C. The weight loss in this temperature range was primarily due to the loss of physisorbed water.³⁸ For all the catalysts, the second step weight loss (17.4–21.4%) was observed in the temperature range of 200–415°C. This loss occurred either may be due to the dissociation of the covalently bonded ligand with the metal complexes or may be because of partial scission of the polymeric chain.³⁹ The third step (405–700°C) weight loss was started immediately after completion of second step and several substeps were also detected. After 700°C, no further weight loss of the

catalysts was observed. The exothermic weight loss of Cu-A, Cu-B, Mn-A, and Mn-B catalysts in third step was 74, 72, 70, and 63%, respectively. In the temperature range of 405–700°C, the loss of weight was significant for all the catalysts due to the decomposition of the metal complexes. At a temperature higher than 700°C, some residue was found may be because of respective metal oxides.

The electronic spectra obtained for the polymer- and nonpolymer-anchored complexes are shown in Figure 5. Methanol was

Table III. TGA Data of Polymer-Anchored Catalysts

Catalyst	Temperature range (°C)	Weight loss (%)	Final residue (%)
Cu-A	85–200	7.8	0.75
	200–405	17.2	
	405–700	74.2	
Cu-B	80–200	7.09	1.87
	200–395	19.1	
	395–700	71.9	
Mn-A	80–200	8.32	0.38
	200–400	21.1	
	400–700	70.2	
Mn-B	90–200	10.7	4.8
	200–415	21.4	
	415–700	63.1	

used as a solvent to collect the spectra of nonpolymer-anchored complexes, whereas nujol mull was used for polymer ligands and polymer-anchored metal complexes. The electronic spectra of nonpolymer-anchored Cu(II) complexes (C-1, C-3) (Figure 5A(a),(b)) exhibited a shoulder band at 372 nm, which corresponded to the ligands to metal charge transfer. A low intensity band was observed at 650 nm, which was corresponded to the d–d transition of Cu(II) complexes. Nonpolymer-anchored Mn(II) complexes (C-2, C-4), exhibited one low intensity band at 600 nm corresponded to d–d transitions (Figure 5B(a),(b)). These transitions were not found in their corresponding polymer-supported Cu(II) and Mn(II) complexes (Figure 5C). This may be due to their poor loading in polymer matrix. However, in nonpolymer-anchored complexes, most of the bands observed within 200–400 nm were due to the ligands, these bands were also observed in polymer-anchored complexes with low intensities (Figure 5C). The electronic spectral results showed that the patterns obtained for nonpolymer- and polymer-anchored complexes were almost close.³² Therefore, square planar structure may also be possible for polymer-anchored complexes, and this is possible only on additional coordination of water/solvent with copper(II).⁴⁰

Catalytic Performance in Styrene Oxidation Over Cu-A Catalyst

Initially, Cu-A catalyst has been chosen, and the styrene oxidation was performed using this catalyst. The effect of various parameters such as temperature, catalyst amount, and styrene to H₂O₂ mole ratio was quantified in terms of conversion and selectivity of different products. The results obtained are shown in Figure 6. Benzaldehyde, styrene oxide, and benzoic acid were observed as the main reaction products and minor amount of phenyl acetaldehyde and 1-phenylethane-1, 2-diol were also detected.

Effect of Mole Ratio of Styrene to H₂O₂. To find the effect of styrene to H₂O₂ mole ratio on the performance of the Cu-A catalyst, the mole ratio of styrene to H₂O₂ was varied from 1 : 1 to 1 : 5. The conversion of styrene over Cu-A catalyst was found to increase with the concentration of H₂O₂ as well as reaction time as shown in Figure 6A. The conversion obtained with the mole ratio of 1 : 4 and 1 : 5 were almost close after a run

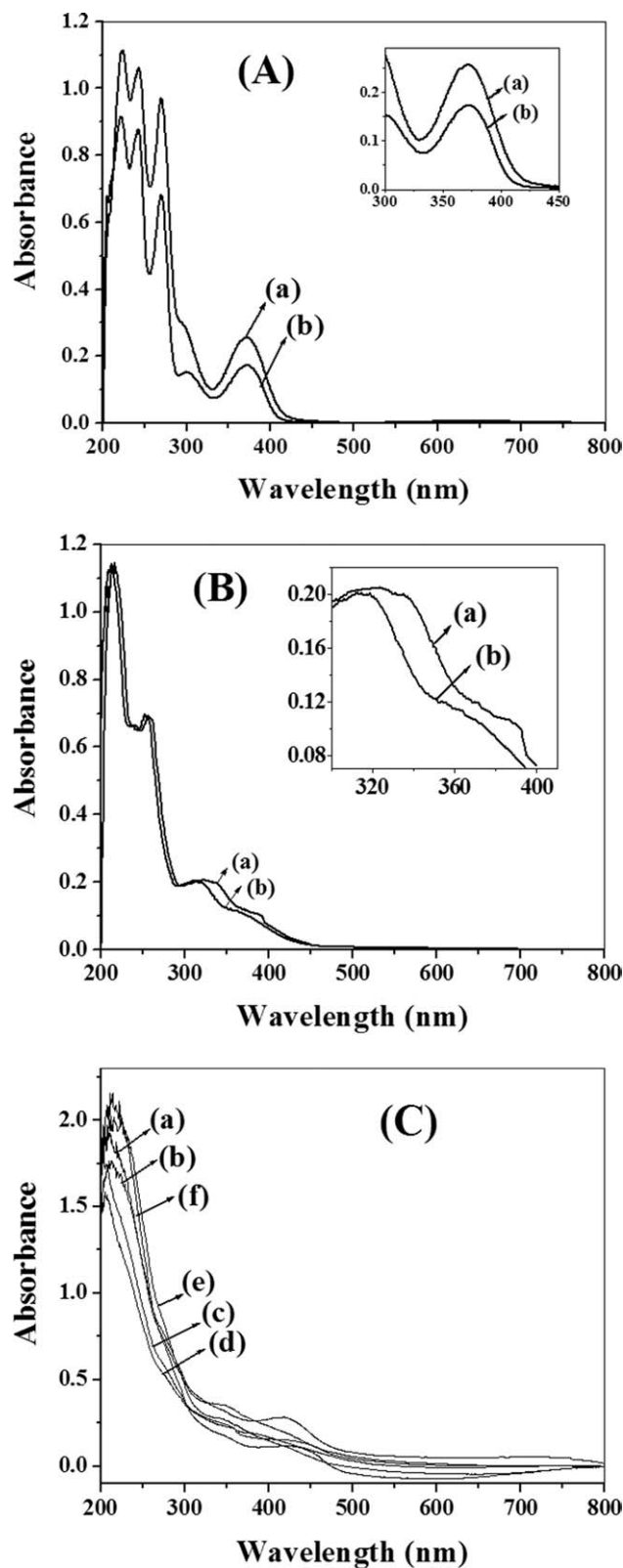


Figure 5. (A) Electronic spectra of nonpolymer-anchored Cu(II) complexes: (a) C-1 and (b) C-3. (B) Electronic spectra of nonpolymer-anchored Mn(II) complexes (a) C-4 and (b) C-2. (C) Electronic spectra of polymer-anchored complexes and ligands: (a) Mn-B, (b) Mn-A, (c) Cu-B, (d) Cu-A, (e) L-1, and (f) L-2.

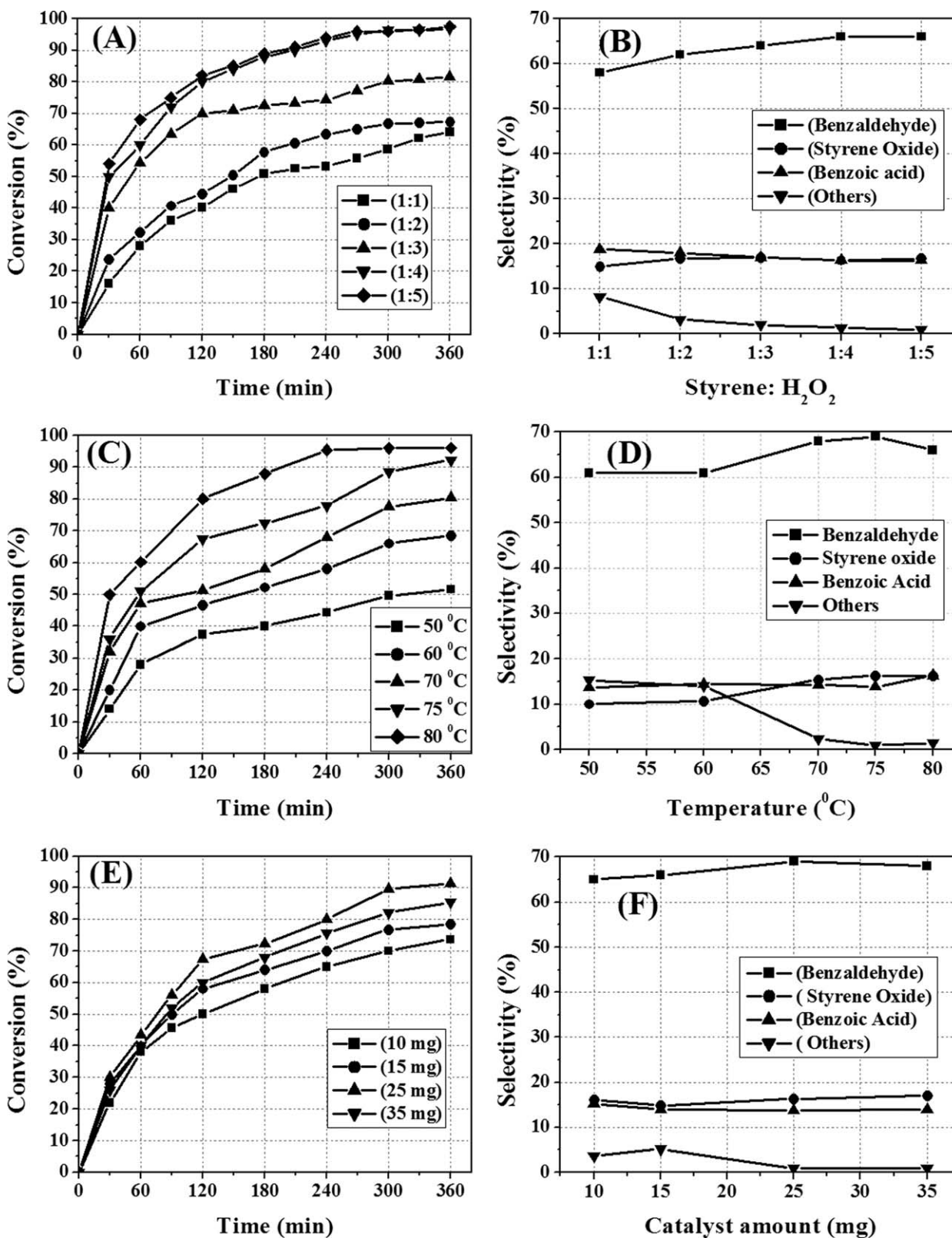


Figure 6. Effect of reaction parameters on conversion and product selectivity over Cu-A catalyst. (A) Effect of styrene conversion with time at different styrene to H₂O₂ mole ratio at 80°C. (B) Selectivity of products at different styrene to H₂O₂ mole ratio at 80°C. (C) Effect of styrene conversion with time at different temperatures at styrene to H₂O₂ mole ratio of 1 : 4. (D) Selectivity of products at different temperatures at styrene to H₂O₂ mole ratio of 1 : 4. (E) Effect of styrene conversion with time at different catalyst amount at styrene to H₂O₂ mole ratio of 1 : 4 and 75°C temperature. (F) Selectivity of products at different catalyst amount at styrene to H₂O₂ mole ratio of 1 : 4 and 75°C temperature.

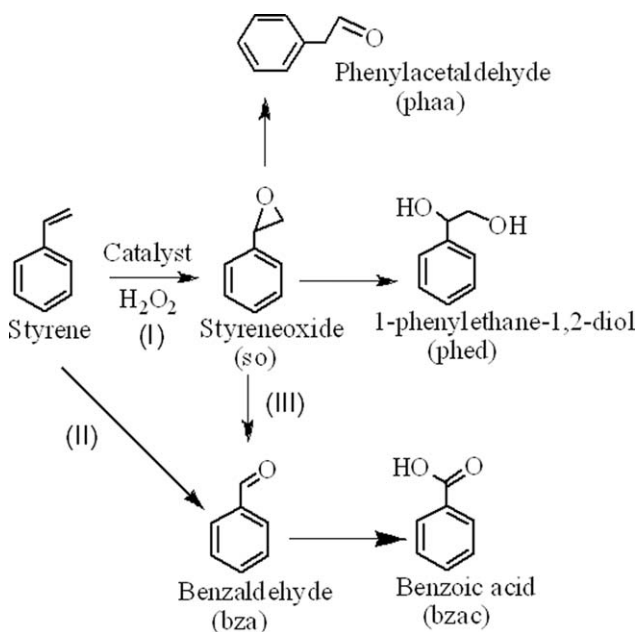


Figure 7. Reaction products of oxidation of styrene.

time of 120 min. The maximum conversion (96%) of styrene was obtained at 80°C after a reaction time of 6 h. Maurya et al.⁴¹ and Guo and coworkers⁴² reported the similar kind of results. With increasing the H_2O_2 concentration in the reaction mixture, the conversion of styrene was increased considerably due to more and more consumptions of H_2O_2 for styrene oxidation. The product formation may take place according to the reaction pathway shown in Figure 7.⁴³ Figure 6B shows the selectivity of different products as a function of styrene to H_2O_2 mole ratio. The selectivity to benzaldehyde was found to increase with H_2O_2 , which varied from 58% (at styrene to H_2O_2 ratio 1 : 1) to 66% (at styrene to H_2O_2 ratio 1 : 4 and above). However, selectivity to styrene oxide and benzoic acid remained almost constant, and selectivity to other products was found to decrease. The conversion and product selectivity data (Figure 6A,B) dictated that the optimum styrene to H_2O_2 ratio was 1 : 4. Therefore, all other catalytic parameters were evaluated at the styrene to H_2O_2 ratio of 1 : 4.

Effect of Temperature. The influence of reaction temperature on styrene oxidation was evaluated by changing the reaction temperature from 30°C (ambient temperature) to 80°C. The experimental data showed that the conversion of styrene was low (~16%) below 50°C. The data obtained in the temperature range of 50–80°C are shown in Figure 6C. For all the experiments, data were collected over a run time of 6 h. Figure 6C shows the effect of temperature variation on overall conversion of styrene with time. The results indicated that conversion of styrene increased with increase in reaction temperature. The maximum conversion of 96% was obtained at 80°C. After a run time of 6 h, the conversion of styrene at 75 and 80°C was almost constant (~96%). Figure 6D shows the selectivity of different products with the temperature over Cu-A catalyst. The results dictated that at all temperatures, selectivity to benzaldehyde was very high ($\geq 60\%$) when compared with the other products ($\leq 15\%$). This is because of formation of benzaldehyde

occurs following the radical mechanism by the direct C=C bond cleavage of styrene at relatively higher temperature ($>50^\circ\text{C}$). The cleavage of C=C bond was more favorable at higher temperature, as a result the selectivity to benzaldehyde was higher. However, below 70°C, the selectivity to all the products was constant, but at 70°C and above, the selectivity to benzaldehyde and styrene oxide was increased with simultaneous decrease in selectivity to other side products. This may be possible due to the shift of reaction mechanism at a temperature of 70°C and higher. To confirm this argument, the reaction rate constant was calculated and plotted against $1/T$ and the resulting plot is shown in Figure 8. The slope of rate constant k vs. $1/T$ plot changed after 70°C, which indicates the change in mechanism of the reaction. Further, activation energy was also calculated at all temperatures using Arrhenius equation. It was found that till 70°C, the value of activation energy was approximately 26.1 kJ/mol; however, after 70°C, the value of activation energy was increased three times (~80.4 kJ/mol). For multiple reactions, a change in activation energy with temperature indicates a shift in the controlling mechanism of reaction.⁴⁴ With increase in temperature, a sharp rise in activation energy indicated that reaction follows a parallel pathway (Figure 8).

The maximum selectivity to benzaldehyde of 69% was observed at 75°C after a reaction time of 6 h. At this condition, the selectivity to styrene oxide, benzoic acid, and other side products were 16.3, 13.8, and 0.9%, respectively. Further increase in temperature caused decrease in selectivity to benzaldehyde due to further oxidation of benzaldehyde to benzoic acid. Since the selectivity to benzaldehyde was reduced above 75°C and selectivity to styrene oxide was unaffected, 75°C was chosen as a reaction temperature for further studies.

Effect of Catalyst Amount. The effect of catalyst amount on styrene oxidation was investigated by changing the catalyst amount from 10 to 35 mg and keeping the temperature and styrene to H_2O_2 ratio constant at 75°C and 1 : 4, respectively. The results obtained are shown in Figure 6E. It was found in general that the

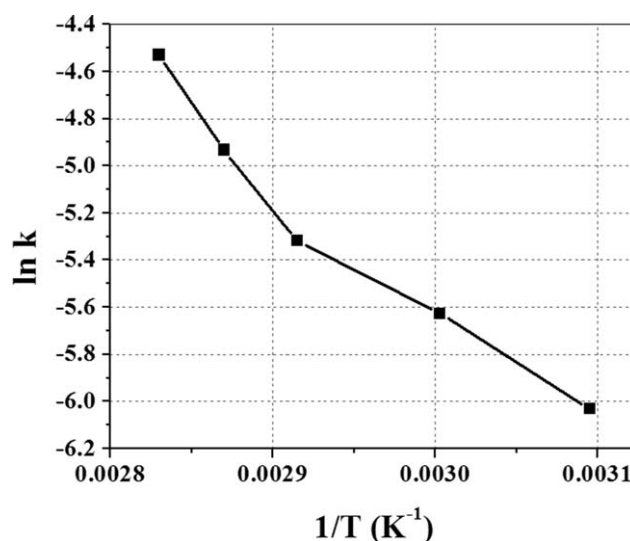


Figure 8. Effect of temperature on rate constant.

Table IV. Conversion of Styrene and Product Selectivity Over Polymer- and Nonpolymer-Anchored Catalysts

Catalysts	Conversion (%)	TOF (h ⁻¹)	Selectivity (%)			
			S _{bza}	S _{so}	S _{bzac}	S _{others}
Without catalyst	8.7	—	87.9	0.0	12.1	0.0
Cu-A	92.3	199.7	69.0	16.3	13.8	0.9
Cu-B	83.4	95.0	68.2	10.2	20.0	1.6
Mn-A	52.7	155.8	84.8	4.9	4.7	5.6
Mn-B	65.4	452.6	76.7	10.5	8.8	4.0
C-1	28.8	38.3	78.4	3.8	10.8	3.7
C-2	32.5	44.6	76.7	6.2	14.3	1.0
C-3	22.4	54.2	84.2	4.3	8.6	1.7
C-4	28.4	38.9	82.3	4.1	12.4	1.2

Reaction conditions: styrene to H₂O₂ mole ratio of 1 : 4, catalyst amount: 25 mg, reaction temperature: 75°C. S_{bza}, selectivity to benzaldehyde; S_{so}, selectivity to styrene oxide; S_{bzac}, selectivity to benzoic acid.

conversion of styrene was increased with reaction time. The effect of catalyst amount on styrene conversion was not very pronounced at reaction time less than 75 min. The effect was more significant beyond the run time of 75 min. With increasing the amount of catalyst from 10 to 25 mg, the overall styrene conversion was increased, whereas with further increase in catalyst amount (>25 mg), the overall conversion was reduced significantly. After the reaction time of 6 h, the maximum conversion of styrene was 92% with 25 mg catalyst whereas conversion reduced to 85% with 35 mg catalyst. Similar kind of activity trend has also been reported in the literature.⁴⁵ One of the possible reasons may be that, in the presence of higher amount of catalyst, the H₂O₂ decomposition rate was higher. Due to higher rate of H₂O₂ decomposition, the concentration of H₂O₂ reduced significantly in the reaction mixture, as a result the styrene conversion was reduced.

The product selectivity obtained with different catalyst amount at the styrene to H₂O₂ mole ratio of 1 : 4 at 75°C after a run time of 6 h is shown in Figure 6E. The product selectivity trend was almost similar as before (Figure 6D). The selectivity to benzaldehyde was found to increase from 65 to 69% with the increase in catalyst amount of 10–25 mg. The selectivity to styrene oxide and benzoic acid was almost unchanged (15%). The selectivity to other products increased slightly with increase in catalyst amount from 10 to 15 mg. With further increase in catalyst amount, the selectivity to the other products was reduced significantly and became almost negligible with 25 mg catalyst and higher. The selectivity trend obtained dictated that the formation of other products was highly affected at higher catalyst amount. The maximum selectivity (69%) to benzaldehyde was found in presence of 25 mg of catalyst. On further increase in catalyst amount up to 35 mg, the selectivity to benzaldehyde was almost constant (Figure 6F). At this condition, the selectivity to styrene oxide and benzoic acid were 16.3 and 13.8%, respectively.

Oxidation of Styrene Over Polymer-Anchored Catalysts (Cu-B, Mn-A, and Mn-B) and Nonpolymer-Anchored Catalysts (C-1, C-2, C-3, and C-4)

The optimum reaction conditions for styrene oxidation has been determined in Section *Catalytic Performance in Styrene*

Oxidation over Cu-A Catalyst, which showed that at styrene to H₂O₂ mole ratio of 1 : 4, temperature 75°C with 25 mg of catalyst, the conversion of styrene was close to 92% after run time of 6 h. At these reaction conditions, the selectivity to benzaldehyde, styrene oxide, and benzoic acid were 69, 16.3, 13.8%, respectively, whereas the selectivity to other side products were almost negligible. Polymer-anchored complex catalysts (Cu-B, Mn-A and Mn-B) and nonpolymer-anchored complex catalysts (C-1, C-2, C-3, and C-4) were tested at these optimum reaction conditions, and the results obtained were compared with the Cu-A catalyst. Turn over frequencies (TOF) for all the catalysts were also calculated. The catalytic results obtained over polymer- and nonpolymer-anchored catalysts are shown in Table IV. The styrene oxidation activity of Cu-A and Cu-B catalyst was higher with respect to the Mn-A and Mn-B. The Cu-B catalyst gave 83.4% conversion with 68.2% selectivity to benzaldehyde whereas Mn(II)-based catalysts, Mn-A and Mn-B gave 52.7% and 65.4% conversion, respectively. The high catalytic activity of Cu(II)-based complexes than Mn(II) may be due to the different type of reaction mechanism of Cu- and Mn-complexes.^{46,47} Therefore, Cu and Mn play an important role during the complex formation, which affected the metal ligand interaction and showed different activity. The activity (83.4%) of Cu-B catalyst was little lower as compared to Cu-A catalyst (92.3%) may be due to the lower TOF and different nature of the ligand (L1). The polymer-anchored Mn-catalysts were less active but it was highly selective to benzaldehyde. The selectivity to benzaldehyde over Mn-A and Mn-B catalysts were 84.8 and 76.7%, respectively. The selectivity to styrene oxide and benzoic acid were also lower as compared to Cu-complexes. Moreover, although Mn-based polymer-anchored catalyst was less active but these catalysts were more selective towards benzaldehyde formation. Therefore, the direct styrene oxidation into benzaldehyde following the reaction path II directly and path I followed by III (Figure 7) was favorable over Mn-complex catalysts.

Nonpolymer-anchored complex catalysts were also tested at the same reaction conditions used for polymer-anchored catalyst for comparison. The results showed that nonpolymer-anchored complex catalysts were the least active catalyst and the activity

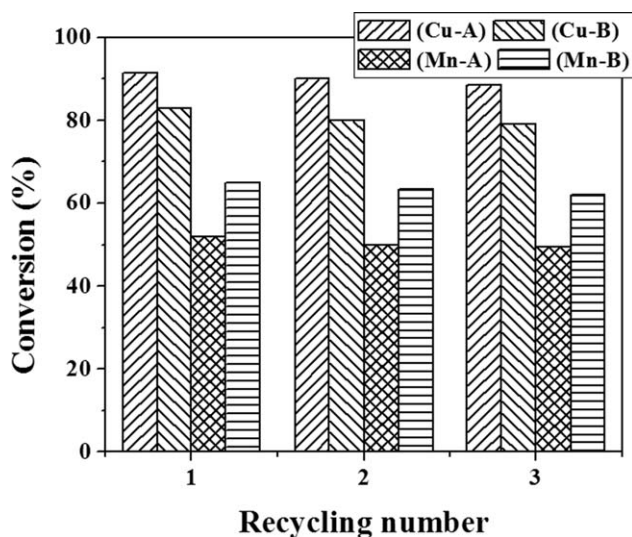


Figure 9. Recyclability of polymer anchored complexes. Reaction conditions: styrene to H_2O_2 mole ratio (1 : 4); catalyst 25 mg; temperature 75°C .

was in the range of 22.4–32.5%. TOF of these catalysts were also significantly low ($38.3\text{--}54.2\text{ h}^{-1}$). The difference in catalytic activity may be due to the difference in their chemical structure. Although, the nonpolymer-anchored catalyst was less active but the selectivity to benzaldehyde was comparable with the polymer-anchored catalysts.

For all the catalysts, selectivity to benzaldehyde was higher because the styrene oxide formed in the first step (reaction path I, Figure 7) may be converted into benzaldehyde by a nucleophilic attack of H_2O_2 to styrene oxide followed by the cleavage of the intermediate hydroperoxystyrene and through the cleavage of $\text{C}=\text{C}$ bond following the reaction path II (Figure 7) simultaneously.^{4,48}

Noncatalytic Oxidation of Styrene

To determine the extent of homogeneous reaction, styrene oxidation was carried out without catalyst at the optimum reaction conditions as obtained over Cu-A catalyst. The results obtained are shown in Table IV. The results showed that in the absence of a catalyst, the styrene conversion was very low (8.7%) with benzaldehyde and benzoic acid selectivity to 87.9 and 12.1 %, respectively.

RECYCLABILITY OF THE CATALYSTS

The recyclability of the Cu-A, Cu-B, Mn-A, and Mn-B catalysts were studied for three cycles over a 6-h reaction period, each at the optimum reaction conditions obtained, and the results are shown in Figure 9. In a typical experiment, the catalyst was filtered after a reaction time of 6 h, thoroughly washed with acetonitrile, and dried at 70°C . These catalysts were tested further under similar reaction conditions. The results showed that there was no appreciable difference in the catalytic activity as well as the product selectivity. The catalytic activity suggested that complexes were stable even after it was used three times, and the selectivity of the products was almost unchanged.

CONCLUSIONS

A series of Cu(II)- and Mn(II)-based polymer- and nonpolymer-anchored complex catalysts for styrene oxidation to benzaldehyde using H_2O_2 as oxidant was investigated. The catalysts were characterized using elemental analysis, FTIR, AAS, EDAX, TGA, and electronic spectral, which confirmed the formation of metal complexes. Polymer-anchored catalysts showed the highest styrene oxidation activity as compared to nonpolymer-anchored complex catalysts. The activity of the polymer-anchored complex catalysts were in the order of $\text{Cu-A} > \text{Cu-B} > \text{Mn-B} > \text{Mn-A}$. The maximum conversion (92.3%) of styrene was obtained over Cu-A catalyst with a styrene to H_2O_2 mole ratio of 1 : 4 at 75°C . At this condition, the selectivity to benzaldehyde was 69%. Although, the Mn-based complex catalysts were less active, these were more selective to benzaldehyde as compared to Cu(II) complex catalysts. Over Mn-A complex catalyst, the maximum selectivity to benzaldehyde was 85% at 52.7% styrene conversion. The catalytic data indicated that Cu(II) complex catalysts propagated the side reaction, which enhanced the side products, whereas Mn(II) complex catalysts suppressed the side reaction and propagated the selective conversion of styrene to benzaldehyde. The nonpolymer-anchored catalysts showed least activity in styrene oxidation. Conversion was in the range of 22.4–32.5%. The selectivity to benzaldehyde over nonpolymer-anchored complex catalysts, however, was comparable (76.7–84.2%) with the polymer-anchored complex catalysts (68.2–84.8%). Therefore, it was concluded that the ligands and the structure of the complexes played a significant role on styrene oxidation. Recyclability test of the polymer anchored catalysts showed that the complexes were stable even after recycling three times. Good recycling efficiency along with high activity and selectivity of polymer-anchored catalysts may be useful for the synthesis of various fine chemicals under environment friendly conditions.

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