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Oxidation of organic compounds by hydrogen peroxide using polymer-anchored azo-metal catalysts

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Abstract Polymer-anchored azo complexes of Cu(II) and Ni(II) were synthesized by the reaction of chloromethylated polystyrene, 3-aminophenol, and 1-nitroso-2-naphthol with the metal chlorides. The catalytic activities of these complexes were studied in the oxidation of various organic substrates including alkenes, alcohols, alkanes, and sulfides with 30 % aqueous hydrogen peroxide. The structures of both catalysts have been investigated by physiochemical methods. Both catalysts proved to be very stable and could be reused more than five times without significant loss of activity. Furthermore, these catalysts require very mild reaction conditions.

Introduction

Hydrocarbon oxidations are essential reactions in organic chemistry, both for basic research and industrial purposes [1, 2]. Oxidations of alkenes and saturated compounds to give the corresponding oxo-products are vital and useful reactions in various industries [3]. The oxidation of alcohols to carbonyl compounds is one of the most fundamental transformations in organic chemistry and also one of the key routes to synthesize benzaldehyde, which is a versatile and widely used synthon in industrial chemistry [4, 5].

Metal complexes are extensively used for the catalytic oxidation of various organic substrates [6, 7]. However, in the work-up processes, homogeneous catalysts face many drawbacks [8, 9]. Hence, the development of heterogeneous catalysts is drawing much current interest. Heterogeneous catalysts are often sufficiently thermally stable to carry out high temperature reactions and can also be easily separated from the products and reused. Therefore, replacement of homogeneous catalysts by heterogeneous catalysts is an important goal in catalysis. The heterogeneous supports may be a range of materials, including alumina [10], amorphous silicates [11], polymers [12], zeolites [13], and functionalized Mobil crystalline materials or functionalized MCM-41 [14].

Functionalized polystyrene-anchored catalysts have been used to carry out various catalytic organic transformations [15, 16]. Polystyrene-anchored transition metal complexes can provide inert and reusable catalysts for the conversion of various organic functional groups [17–19]. In this study, we report our initial efforts on the development of a catalytic system which can oxidize organic substrates under mild conditions. We chose hydrogen peroxide as an oxidant because of its low toxicity [20]. We have developed and characterized a polymer-supported Cu(II)-azo catalyst (Cat-1) and Ni(II)-azo catalyst (Cat-2), and their catalytic performances have been investigated in the liquid-phase oxidation of a variety of organic substrates using 30 % H_2O_2 as oxidant in acetonitrile medium. The effects of different parameters have been investigated in order to optimize the reaction conditions. We have also investigated the effect of reuse of the catalysts on their performance.

Experimental

Analytical-grade reagents and freshly distilled solvents were used throughout the experiments. Liquid substrates were pre-distilled and dried with the appropriate molecular

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sieve. Purification of the solvents and substrates was done by standard procedures [21]. 3-aminophenol, 1-nitroso-2-naphthol, and chloromethylated polystyrene were supplied by Sigma-Aldrich. Other reagents were obtained from Merck.

A Perkin-Elmer 2400 C elemental analyzer was used to collect microanalytical data (C, H, and N). FTIR spectra were recorded on a Perkin-Elmer FTIR 783 spectrophotometer using KBr pellets. A Mettler Toledo TGA/SDTA 851 instrument was used for the thermogravimetric (TGA) analysis. Morphologies of the functionalized polystyrene and complexes were analyzed using a scanning electron microscope (SEM, ZEISS EVO40, England) equipped with EDAX facility. Metal content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS).

Preparation of the catalyst

Synthesis of polymer-anchored ligand (A)

3-aminophenol (0.720 g) was reacted with chloromethylated polystyrene (1.2 g, 5.5 mmol/g Cl) plus NaH (0.200 g) in DMF (10 mL) at 0 °C with continuous stirring for 2 h. The mixture was then left stirring and warming to room temperature over 8 h. The resulting brown mixture was filtered and the residue (pale brown) was washed with ethanol until the filtrate became colorless, then dried under vacuum to get PS-compound (A) (1.7 g).

Synthesis of polymer-anchored azo ligand (B)

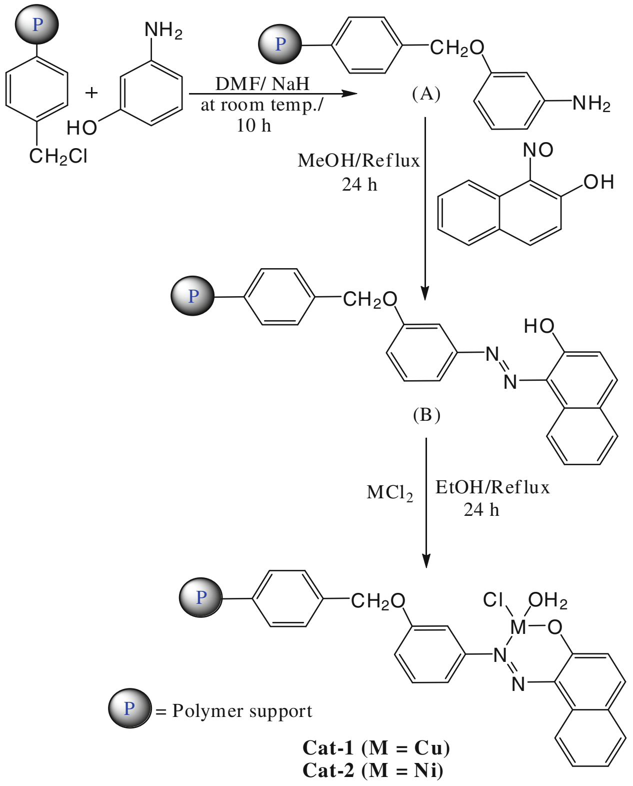
Polymer A (1.2 g) was added to a solution of 1-nitroso-2-naphthol (1.2 g) in MeOH (10 mL) and the mixture was heated to reflux with continuous stirring. The mixture was then cooled to room temperature and filtered. The brown beads were washed with ethanol until the filtrate became colorless and dried under vacuum to give B (1.9 g).

Synthesis of the polymer-anchored complexes

The polymer-anchored azo ligand B (1 g) was suspended in ethanol (20 mL). To this mixture, 5 mL of a 1 % (w/v) ethanolic solution of the appropriate metal chloride ($CuCl_2$/$NiCl_2$) was added dropwise over a period of 30 min under constant stirring. The resulting mixture was refluxed for 24 h. The resulting solid mixture was filtered off, washed thoroughly with ethanol, and dried at room temperature under vacuum and give the PS-Cu(II)-azo complex (Cat-1, 1.04 g) or PS-Ni(II)-azo complex (Cat-2, 1.03 g).

Procedure for catalytic oxidation

A mixture of catalyst (0.1 mmol), MeCN (10 mL), and substrate (5 mmol) was stirred vigorously at 60 °C in a 50-mL two-necked round-bottom flask equipped with a condenser. H_2O_2 (10 mmol of 30 % aqueous solution) was



Scheme 1 Preparation of the polymer-anchored complexes

Table 1 Elemental analysis

Compound	C (%)	H (%)	N (%)	Cl (%)	Metals (%)
PS-compound (A)	79.08 (80.40)	6.44 (6.70)	5.05 (6.01)	3.08	–
PS-azo ligand (B)	78.02 (79.21)	5.49 (5.31)	6.20 (7.22)	2.23	–
PS-Cu(II)-azo complex	69.30 (60.96)	5.37 (4.88)	5.48 (5.56)	5.57	5.79
PS-Ni(II)-azo complex	69.81 (61.54)	5.39 (4.92)	5.52 (5.61)	5.61	4.98

Expected values are given in parenthesis

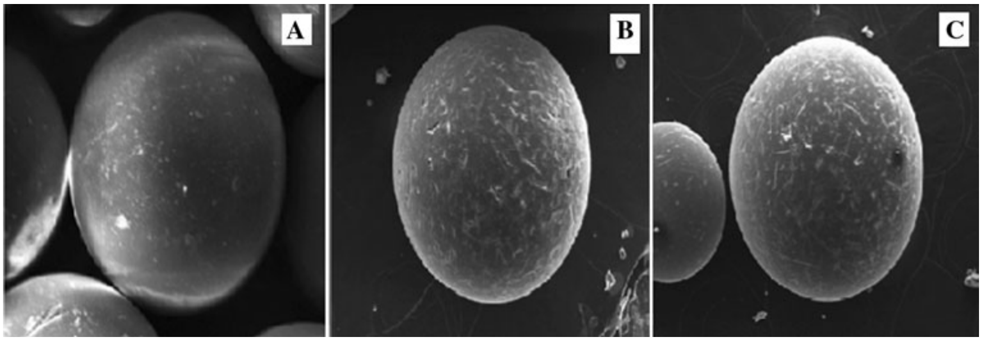


Fig. 1 FE SEM image of polymer-anchored azo ligand (**a**) and polymer-anchored complexes Cat-1 and Cat-2 (**b**, **c**)

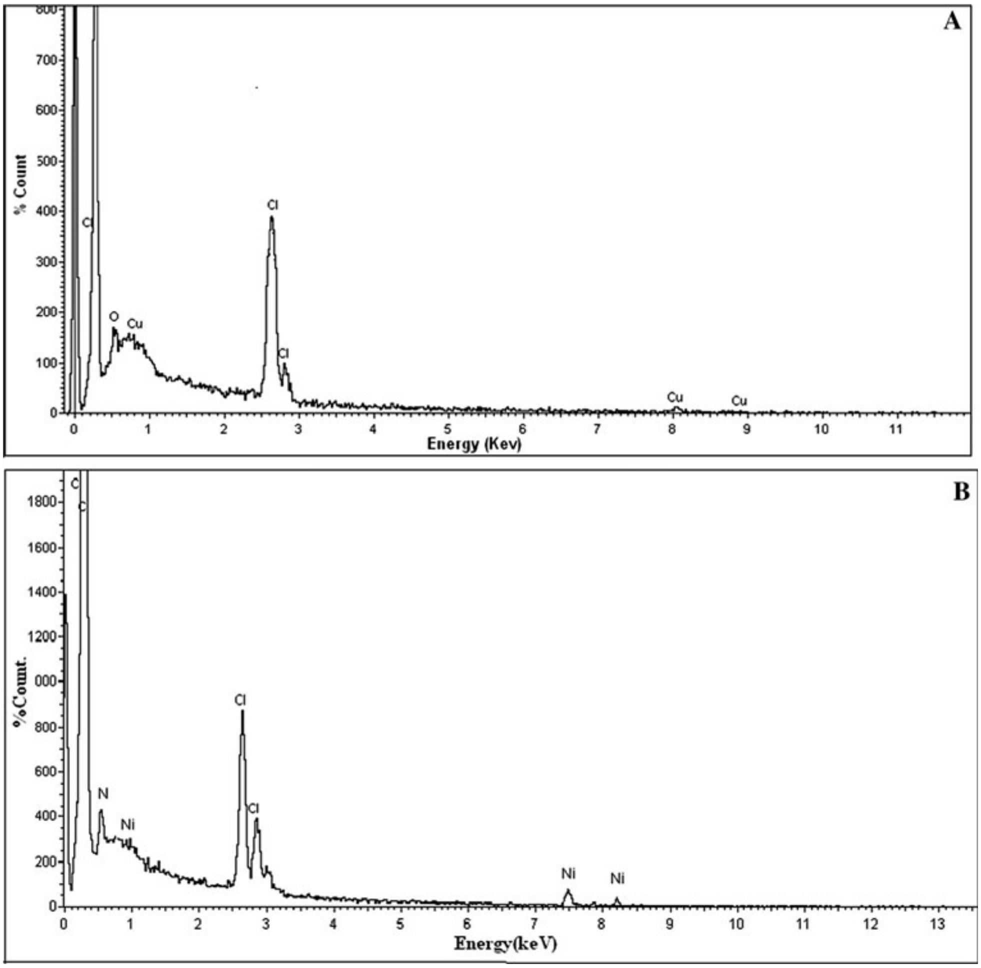


Fig. 2 EDAX data polymer-anchored complexes Cat-1 and Cat-2 (**a**, **b**)

added in three portions over 3 h. The resulting mixture was then stirred at 60 °C for 8 h. After filtration, the filtrate was concentrated and then analyzed using a Varian 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and flame ionization detector. The products were determined using cyclohexanone as internal standard. All reaction products were identified using an Agilent GC–MS.

Results and discussion

Characterization of the polymer-anchored complexes

Owing to the insolubilities of these polymer-supported metal complexes in organic solvents, their structural characterization was limited to their physicochemical properties, chemical analysis, SEM, TGA, FTIR, and UV–

Table 2 IR stretching frequencies of polymer-anchored azo ligand and complexes

Compound	Color	IR (cm^{-1}, KBr[a])					
		NH_2 (primary)	M–O	N=N	M–N	O–H	C–O
PS-compound (A)	Pale brown	3,463	–	–	–	–	1,370
PS-azo ligand (B)	Brown	–	–	1,452	–	3,401	1,370
PS-Cu(II)-azo complex	Green	–	642	1,440	533	–	1,357
PS-Ni(II)-azo complex	Greenish brown	–	640	1,440	513	–	1,357

[a] Infrared spectra measured as KBr pellets

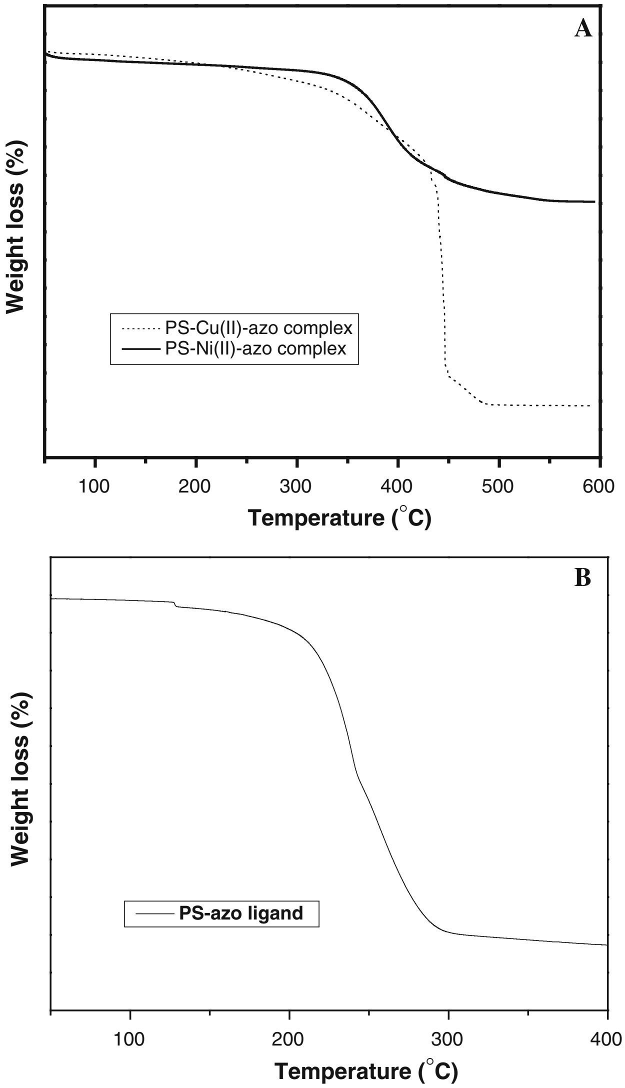


Fig. 3 Thermal studies of polymer-anchored complexes Cat-1 and Cat-2 (**a**) and polymer-anchored azo ligand (**b**)

Vis spectroscopic data. Table 1 provides the elemental analysis data. The metal contents of the supported catalysts (5.79 % for the Cu complex and 4.98 % for the Ni complex) were estimated by atomic absorption spectrometry.

The outline for the preparation of polymer-anchored azo complexes is given in Scheme 1.

Scanning electron micrograph (SEM) images of the polymer-supported azo ligand and its transition metal complexes were recorded to understand the morphological changes occurring on the surface of the polymer matrix. Figure 1 shows the SEM images of the polymer-anchored azo ligand (Fig. 1a) and the immobilized Cu(II) and Ni(II) complexes (Fig. 1b, c, respectively). The original polymer beads have a smooth and flat surface (not shown in Fig. 1). The introduction of the ligand onto the polystyrene beads causes a roughening on the surface layer. Images of the metal complexes show further roughening on the surface. Energy dispersive spectroscopy X-ray (EDX) analyses of the complexes show the expected metal content along with C, N, O, and Cl, consistent with the formation of the metal complexes (Fig. 2). The ratios of metals and other elements obtained from EDX analysis are quite similar to the data obtained from elemental analysis (Table 1). The presence of the metals is confirmed by energy dispersive spectroscopy analysis of X-rays (EDAX).

The mode of attachment of the transition metals onto the support was confirmed by the comparison of the FTIR spectral bands of the polymers before and after loading with metals, both in the mid (4,000–400 cm^{-1}) and far (600–50 cm^{-1}) IR regions (Table 2). The IR spectrum of pure chloromethylated polystyrene has an absorption band at 1,261 cm^{-1} due to the presence of the C–Cl group, which was absent in the spectra of the anchored ligand and the catalysts. The IR spectra show a stretching vibration for CH_2 at 2,918 cm^{-1} for the polymer bound ligand and its complexes. The N=N stretches were observed at 1,452 cm^{-1} for the polymer bound azo ligand and 1,440 cm^{-1} in the two metal complexes, indicating the coordination of nitrogen to the metal. Bands at 3401 (only in B) and 1,370 cm^{-1} (in both A and B) have been assigned to the stretching vibrations of the frequency of phenolic –OH and free C–O stretches, respectively. In the PS-M(II)-azo complexes, a new peak at 1,357 cm^{-1} can be attributed to a shift in the C–O stretch as a result of coordination through the phenolic oxygen [22]. The M–O peaks for the metal complexes are observed around 630–680 cm^{-1} [23]. In the far IR, bands due to the M–N stretching vibration are observed at 520–580 cm^{-1} [23],

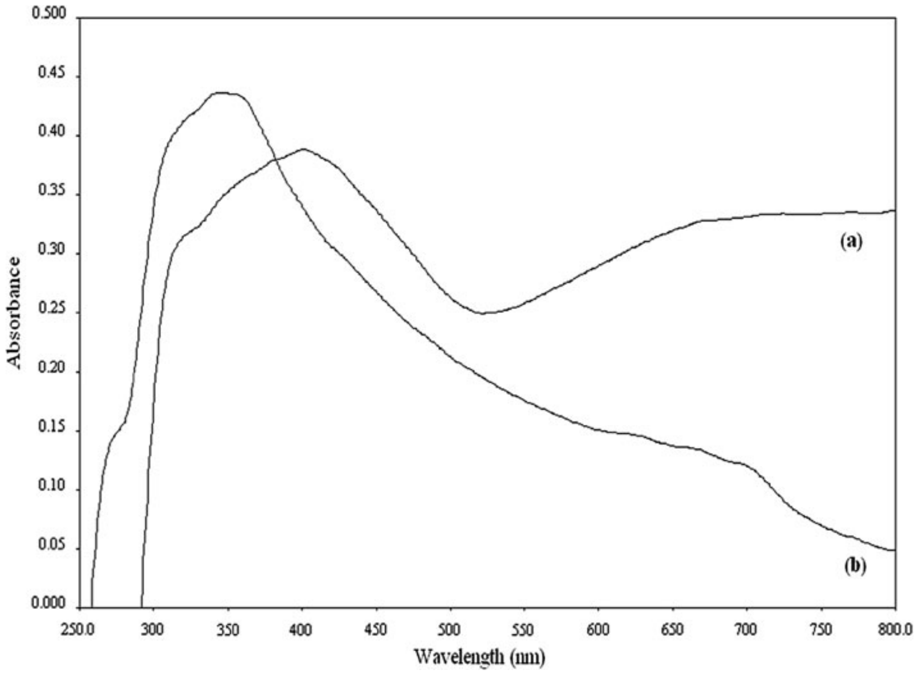
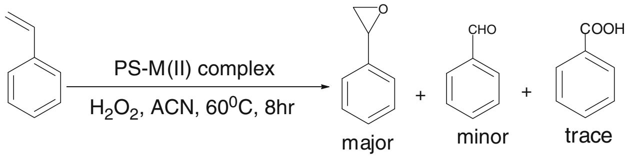


Fig. 4 DRS-UV–visible absorption spectra of polymer-anchored complexes Cat-1 (**a**) and Cat-2 (**b**)



Scheme 2 Oxidation of styrene

Table 3 Styrene oxidation using different solvents with Cat-1 and Cat-2

Sl. No.	Solvent	Conversion (%)[a]	Selectivity of styrene oxide (%)[a]	
		(PS-Cu(II)-azo/PS-Ni(II)-azo)	PS-Cu(II)-azo	PS-Ni(II)-azo
1	Toluene	Nil	Nil	Nil
2	MeOH	20/12	40	31
3	H_2O	52/41	52	44
4	ACN	95/82	90	79
5	DMSO	76/63	72	63

Reaction conditions: catalyst (0.1 mmol), styrene (5 mmol), solvent (10 mL), H_2O_2 (10 mmol), 60 °C, time: 8 h

[a] Determined by GC

which supports the formation of the metal complexes through M–N bonds. The metal complexes also show a characteristic (Cu–Cl) frequency at 314 cm^{-1} [24] and (Ni-Cl) frequency at 247 cm^{-1}.

The thermal stabilities of the complexes were investigated using TGA at a heating rate of 10 °C/min in air over a temperature range of 50–600 °C. The TGA curves are shown in Fig. 3. For the polymer-supported Cu(II) complex, decomposition started at around 290–300 °C, whereas the Ni(II) complex decomposed at 330–380 °C. Hence, these polymer-supported metal complexes degrade at fairly high temperatures and the Ni(II) complex is the most thermally stable.

The electronic spectra (Fig. 4) of the supported metal complexes were recorded in diffuse reflectance spectrum mode as $MgCO_3/BaSO_4$ discs, due to their solubility limitations in common organic solvents. Cat-1 and Cat-2 exhibit bands around 310–440 and 300–400 nm, respectively, which may be assigned to $\pi \rightarrow \pi^*$ transitions of intra-ligand charge transfer of the benzenoid moiety and $n \rightarrow \pi^*$ transition of the azo group.

Catalytic oxidation of styrene

Oxidation of styrene, catalyzed by both supported complexes using H_2O_2 as an oxidant, gives styrene oxide as major product, as shown in Scheme 2. We have optimized the reaction conditions by varying different parameters, namely the amount of oxidant, amount of catalyst, and temperature. The epoxidation of styrene was also examined using different solvents. Table 3 shows the influence of solvents on the conversion of styrene and yields of styrene oxide for the two catalysts. Acetonitrile proved to be the best solvent for these reactions. An interesting result is that the PS-Cu(II)-azo catalyst is more efficient than the PS-Ni(II)-azo catalyst.

The effects of different oxidants like TBHP, H_2O_2, PhIO, and $KHSO_5$ with these catalysts have also been examined. The results are given in Table 4. Hydrogen

Table 4 Oxidation of styrene using different oxidants with Cat-1

Sl. No.	Oxidant	Conversion (%)[a] (PS-Cu(II)-azo/ PS-Ni(II)-azo)	Yield (%)[a] (Styrene oxide/ Benzaldehyde)	
			PS-Cu(II)-azo	PS-Ni(II)-azo
1	None	Nil	Nil/Nil	Nil/Nil
2	PhIO	71/62	35/30	23/35
3	K_2SO_5	76/69	40/27	30/32
4	TBHP	79/70	63/12	53/14
5	H_2O_2	95/82	86/7	65/11

Reaction conditions: catalyst (0.1 mmol), styrene (5 mmol), ACN (10 mL), oxidant (10 mmol), 60 °C, time: 8 h

[a] Determined by GC

peroxide proved to be the most suitable oxidant for both catalytic systems. Again, that copper catalyst is more active than the nickel catalyst.

To determine the optimum reaction temperature, we studied the epoxidation of styrene at temperatures between 40 and 70 °C, using H_2O_2 as oxidant and acetonitrile as solvent (Fig. 5). We found 60 °C to be the optimum reaction temperature; at higher temperatures, the selectivity for styrene oxide decreases due to decomposition.

Next, three different amounts, specifically 0.05, 0.1, and 0.2 mmol of catalyst, have been used under the above reaction conditions. Using 0.05 mmol of catalyst, conversion was only 65 % while using 0.1 and 0.2 mmol of catalyst conversions reached 95 and 96 %, respectively. Hence, 0.1 mmol of PS-Cu(II) catalyst is sufficient to carry out the reactions.

To find the optimum ratio of substrate to oxidant, 1:1, 1:2, and 1:3 ratios were investigated with styrene (10 mmol) and catalyst (0.1 mmol) in acetonitrile (10 mL), at 60 °C. As illustrated in Fig. 6, the conversion of styrene improved from 52 to 95 % upon increasing the styrene to aqueous 30 % H_2O_2 molar ratio from 1:1 to 1:2, though selectivity at 1:1 ratio was high. The conversion remained nearly constant upon further increasing the ratio to 1:3, but the selectivity toward styrene oxide decreased; hence, a large amount of oxidant is not an essential condition to improve the selectivity for this reaction.

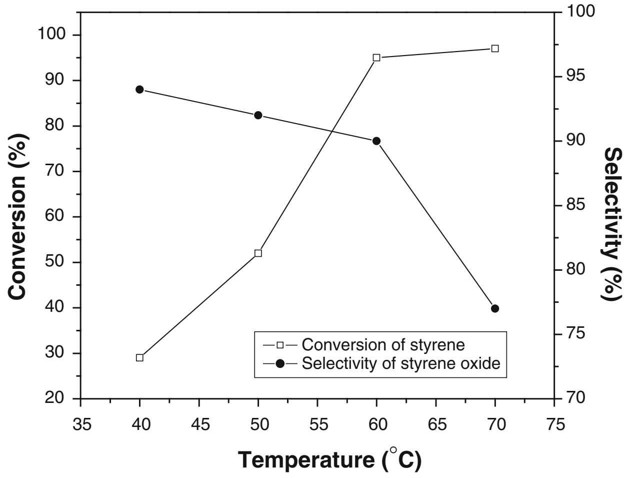


Fig. 5 Effect of temperature on the oxidation of styrene using Cat-1. Reaction condition: styrene (5 mmol), ACN (10 mL), H_2O_2 (10 mmol), catalyst (0.1 mmol)

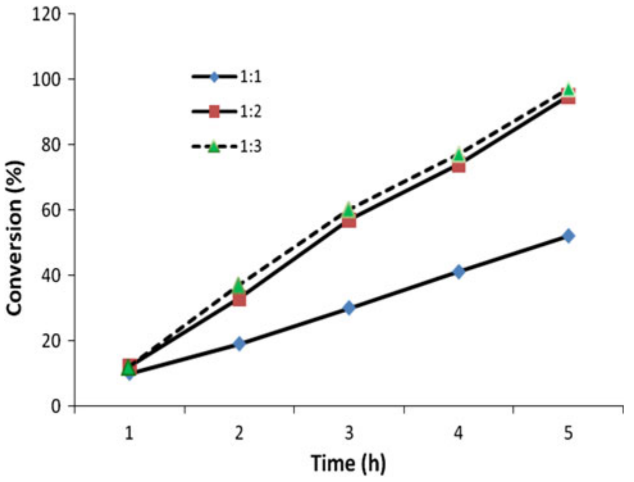


Fig. 6 Effect of substrates-to-oxidant molar ratio on oxidation of styrene as a function of time using Cat-1. Reaction condition: Styrene (5 mmol), ACN (10 mL), catalyst (0.1 mmol), temperature = 60 °C and time = 8 h

In summary, we find the optimized reaction conditions for the oxidation of styrene are; substrate 5 mmol, catalyst 0.1 mmol, substrate/oxidant ratio 1:2, solvent (acetonitrile) 10 mL, and temperature 60 °C. The PS-Ni(II) complex was less reactive than the PS-Cu(II) catalyst under the optimized reaction conditions. Next, we studied the activities of the catalysts with other olefins. Cyclic olefins such as limonene and α-pinene are oxidized with high selectivity (81 and 83 %), and generally similar results were obtained (Table 5).

Oxidation of other substrates

In order to explore further the catalytic activity and selectivity of these catalysts, oxidations of alkanes, alcohols, and sulfides were investigated under the optimum reaction conditions, with some excellent results (Table 6). Ethylbenzene was transformed into acetophenone in up to 75 % yield. The catalysts also gave good results with the substituted benzyl alcohols and sulfides.

It is clear from Tables 5 and 6 that olefins are selectively oxidized to their corresponding epoxides, while alkanes and alcohols are selectively oxidized to aldehydes or ketones, and sulfides are selectively oxidized to their corresponding

Table 5 Oxidation of Olefins using Cat-1 and Cat-2

SL. No.	Olefins	Conversion (%)[a] (PS-Cu(II)-azo/ PS-Ni(II)-azo)	Selectivity of the epoxide (%)[a] (PS-Cu(II)-azo/ PS-Ni(II)-azo)
1	Styrene	95/72	90/76
2	p-Methylstyrene	90/79	80/68
3	p-Metoxystyrene	84/66	87/78
5	α-Pinene	66/53	81/69
6	Limonene	62/49	83/72
7	Cyclohexene	87/76	91/79
8	Cyclooctene	80/68	88/74

Reaction conditions: catalyst (0.1 mmol), substrate (5 mmol), ACN (10 mL), oxidant (10 mmol), 8 h, 60 °C

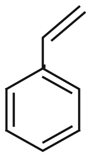
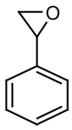
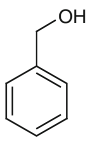
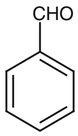
[a] Determined by GC and GC–MS

sulfoxides. Comparison of our results with other reported catalysts (Table 7) reveals that the present system gives better conversions than other catalysts.

Heterogeneity and recycling tests

To check that the catalyst is actually functioning in a heterogeneous manner, a hot-filtration test was performed on the oxidation reaction. During the catalytic oxidation of styrene, the solid catalyst was separated from the reaction mixture by filtration after 4 h of reaction and the obtained filtrate was continually stirred under the same reaction conditions for a further 3 h. Gas chromatographic analysis showed no increment in the conversion, and atomic absorption spectrometric analysis of the filtrate confirmed that no metals were present in the reaction mixture. The metal content of the recycled catalysts was also unaltered, indicating no leaching of the metal from the polymer support during the catalytic oxidation reactions.

Table 7 Comparison of polymer-anchored complex catalysts Cat-1 and Cat-2

Substrates	Catalysts	Conversion (%)		Reference
	Cat.1	95	 90	This work
	Cat-2	72	76	This work
	PS-[Cu(ligand)$_n$]	57	3.6	25
	Cat.1	96	 90	This work
	Cat.2	81	83	This work
	PyC4	93.6	90.5	26

The recyclability of the catalysts was studied in repeated styrene oxidation reactions (Table 8). The catalysts were separated from the reaction mixture after each experiment

Table 6 Oxidation of different substrates using Cat-1 and Cat-2

Sl. No.	Substrate	Conversion (%)[a]	Selectivity of the product (%)[a]		
		(PS-Cu(II)-azo/PS-Ni(II)-azo)	(PS-Cu(II)-azo/PS-Ni(II)-azo)		
			Aldehyde	Ketone	Sulfoxide
	Alkanes				
1	Ethylbenzene	75/62	–	79/59	–
2	Toluene	35/21	100/79	–	–
	Alcohols				
3	Benzyl alcohol	96/81	90/83	–	–
4	4-Methylbenzyl alcohol	94/76	89/74	–	–
5	4-Nitrobenzyl alcohol	87/69	91/80	–	–
6	4-Bromobenzyl alcohol	92/78	86/72	–	–
	Sulfides				
7	1-Propenphenyl sulfide	91/83	–	–	98/79
8	Di-phenyl sulfide	90/76	–	–	100/82
9	Di-methyl sulfide	87/74	–	–	91/78

Reaction conditions: catalyst (0.1 mmol), substrate (5 mmol), ACN (10 mL), oxidant (10 mmol), 8 h, 60 °C

[a] Determined by GC and GCMS

Table 8 Recycling efficiency of the catalysts for the oxidation of styrene

Reuse time	Conversion (%)[a]	
	Cat-1	Cat-2
First time	95	80
Second time	93	79
Third time	92	77
Fourth time	91	76
Fifth time	90	75

Reaction conditions: catalyst (0.1 mmol), substrate (5 mmol), ACN (10 mL), oxidant (10 mmol), 8 h, 60 °C

[a] Determined by GC

by filtration, washed with methanol, and dried carefully before reuse in subsequent runs. After five consecutive uses of the catalyst, the styrene conversion was 85 %. The recovered catalysts showed no change in their IR and UV–vis spectra. Hence, the nature and activity of the catalyst was not significantly altered after five repeat runs.

Conclusion

Polymer-anchored azo-metal complexes of Cu(II) and Ni(II) have been synthesized and characterized by spectrophotometric methods. The catalytic activities of these complexes were tested for the liquid-phase oxidation of olefins using hydrogen peroxide as the oxidant. Excellent conversion and selectivity toward the oxidation of olefins, aromatic alcohols, alkanes, and sulfides were observed. These polymer-anchored catalysts are easy to prepare, air-stable, and inexpensive solids. Easy product recovery and recycling efficiency along with high selectivity of these catalysts may be useful for the synthesis of different fine chemicals under mild conditions.

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