Use of immobilized transition metal complexes as recyclable catalysts for oxidation reactions with hydrogen peroxide as oxidant

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Abstract A tetradentate Schiff base (teta), obtained from triethylenetetramine and salicylaldehyde, has been covalently bonded to divinylbenzene cross-linked chloromethylated polystyrene. This chelating ligand, abbreviated as PS-teta (PS = polymeric support), reacts with metal chlorides (Cu²⁺, Co²⁺, and Ni²⁺) in methanol to give polymerbound transition metal complexes, PS-Cu(II)teta/(Cat-1), PS-Ni(II)teta/(Cat-2), and PS-Co(II)teta/(Cat-3), formation of which has been established by various physiochemical methods and spectroscopic techniques. The catalytic potential of these materials has been tested for the oxidation of various alkenes, alkanes, alcohols, and thioethers in the presence of 30% H₂O₂ as an oxidant. At the same time, these catalysts are very stable and could be reused in oxidation reactions for more than five times without noticeable loss of their catalytic activity.

Introduction

The oxidation of hydrocarbons to oxygenic compounds is a pivotal reaction in organic chemistry, for both fundamental research and industrial manufacturing [1, 2]. Oxidation of olefins and alkanes to give oxygen containing value-added products like alcohols, aldehydes, ketones, acids, and epoxides is an extremely important and useful reaction in both chemical and pharmaceutical industries [3]. Similarly, the oxidation of primary and secondary alcohols to carbonyl compounds is one of the simplest and most useful

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transformations in organic chemistry. The oxidation of benzyl alcohol to benzaldehyde is an important organic transformation, since benzaldehyde has applications in the perfume, pharmaceutical, dyestuff, and agrochemical industries [4, 5].

Now, from both economic and environmental points of view, much attention has recently been focused on the catalytic oxidation of organic compounds using metal catalysts. Transition metal complexes are widely used in homogeneous and heterogeneous catalytic oxidations of different alkenes, alkanes, alcohols, thioethers, etc. [6, 7]. In the recent past, there has been an increasing interest in developing environmental-friendly greener processes, which are also economically viable. Homogeneous transition metal catalyst systems suffer from a major drawback of the catalyst recovery and/or reuse affecting the overall economics of the process [8, 9]. Through the past few decades, there have been significant developments in the application of heterogeneous catalysts for the industrial production of organic chemicals. Heterogeneous catalysts, which are widely used in industry, have good thermal stability, can be easily separated from the reaction mixture, and can be often regenerated and reused. Therefore, heterogenizing of a homogeneous metal complex by supporting it on an insoluble support has attracted a lot of interest as a suitable method for solving many practical problems including the recovery of the catalyst from reaction mixtures and recycling. Transition metals supported on materials such as alumina [10], amorphous silicates [11], polymers [12] and zeolites [13], and MCM-41 [14] are commonly in use in heterogeneous catalysis.

Polystyrene is one of the most frequently studied heterogeneous supports due to its environmental stability and good catalytic activity. Polymer-supported transition metal catalysts derived from functionalized polystyrene resin

have been employed in various organic reactions [15, 16]. This encourages us to investigate the functionalized polystyrene resin-supported transition metal complexes for oxidation reactions. We have already reported the use of a polystyrene-anchored transition metal complex as an airstable, active, and reusable catalyst in various organic reactions [17–19]. In the present study, our initial efforts have focused on developing a 'green' catalytic oxidation system that employs hydrogen peroxide, an eco-friendly oxidant whose only oxidation by-product is water [20]. Hydrogen peroxide is a very attractive oxidant due to ready availability, high oxygen content, and ease of use. Here, we have developed and characterized a polymer-supported Cu(II) complex of a Schiff base ligand [PS-Cu(II)teta] catalyst, and catalytic performances are investigated in the liquid-phase oxidation of various alkenes, alkanes, alcohols, and thioethers using 30% H₂O₂ as oxidant in acetonitrile medium with excellent conversion and selectivity for the value-added products like organic epoxides, sulfoxides, acetophenone, and benzaldehyde. The effects of different experimental parameters are investigated in order to optimize the reaction conditions. We have also compared the catalytic activity of the polymer-supported catalyst with its cobalt and nickel analogs [PS-Co(II)teta, PS-Ni(II)teta]. The catalytic activities were also tested with recycled catalyst. The catalytic activity and selectivity of products did not decrease notably during the recycling experiments.

Experimental

Analytical-grade reagents and freshly distilled solvents were used throughout the experiment. Liquid substrates were predistilled and dried by appropriate molecular sieve. Distillation and purification of the solvents and substrates were done by standard procedures [21]. Salicylaldehyde, triethylenetetramine, and chloromethylated poly(styrenedivinyl benzene) were supplied by Sigma-Aldrich chemicals Company, USA. Other reagents were obtained from Merck Co.

A Perkin-Elmer 2400 C elemental analyzer was used to collect microanalytical data (C, H, and N). FTIR spectra of the samples 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

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

Preparation of Schiff base compound (A)

Triethylenetetramine was reacted with salicylaldehyde (in 1:2 molar ratio) in methanol solvent at 70 °C with stirring for 24 h to prepare the yellow Schiff base compound. The mixture was cooled to room temperature and then filtered. The residue was washed with ethanol until the filtrate became colorless and dried under vacuum.

Preparation of polymer-bound ligand (B)

The polymer-anchored ligand was prepared as follows: Chloromethylated polystyrene (1.2 g) was added to a methanolic solution of Schiff base compound (1 g) and heated to reflux with continuous stirring. After refluxing, the mixture was cooled to room temperature and then



Scheme 1 Preparation of polymer-anchored Schiff base complexes

filtered. The yellow beads were washed with ethanol until the filtrate became colorless and dried under vacuum.

Preparation of polymer-bound Cu(II), Ni(II), and Co(II) complexes (Cat-1, 2, and 3)

Polymer-anchored Schiff base ligand (1 g) was taken in ethanol (20 mL). To the reaction mixture, 5 mL of 1% (w/ v) ethanolic solution of metal chlorides (CuCl₂, NiCl₂, or CoCl₂) was added dropwise over a period of nearly 30 min under constant stirring. Then, the reaction mixture was refluxed for 24 h. The complexes thus formed were filtered off and washed thoroughly with ethanol and dried at room temperature under vacuum.

Procedure for catalytic oxidation

A mixture of 0.1 mmol of catalyst, 10 mL of solvent (MeCN), and 5 mmol of substrates was stirred in a 50-mL two-necked round-bottom flask equipped with a condenser and placed in an oil bath at 60 °C temperature under vigorous stirring, and 10 mmol of H_2O_2 (30% aqueous solution) was added in three intervals. The resulting mixture was then stirred for 8 h. After filtration, the filtrate was concentrated and then analyzed by Varian 3400 gas chromatograph equipped with a 30-m CP-SIL8CB capillary column and a flame ionization detector. The products were determined using cyclohexanone as internal standard. All reaction products were identified by using an Agilent GC–MS.

Results and discussion

Characterization of polymer-bound metal Schiff base complexes

The Schiff base ligand obtained from salicylaldehyde and triethylenetetramine was well characterized and established earlier [22]. Due to the insolubilities of the polymer-supported metal complexes in all common organic solvents, their structural investigation was limited to their physicochemical properties, chemical analysis, SEM, TGA, FTIR, and UV–Vis spectral data. Table 1 provides the data of elemental analysis. Elemental analysis indicates that all of the complexes are monomeric, being formed by the coordination of 1 mol of metal and 1 mol of Schiff base ligand. The metal content of the polymer-supported catalysts was estimated by atomic absorption spectrometer. The chemical composition confirmed the purity and stoichiometry of the neat and polymer-supported complexes.

Scanning electron micrographs (SEM) and energydispersive X-ray analyses (EDAX)

Scanning electron micrographs of the polymer-supported Schiff base ligand and prepared transition metal complexes were recorded to understand the morphological changes occurring on the surface of the polymer matrix. In Fig. 1, the SEM images of the polymer-anchored ligand (Fig. 1a) and the immobilized Cu(II), Ni(II), and Co(II) complexes on modified polystyrene (Fig. 1b-d) are shown. SEM pictures showed the morphological difference between the ligand and the catalysts. Pure 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 top layer. Images of the metal complexes show further roughening on the top layer, which may be due to the interaction of the metal atoms with the ligand to accommodate the fixed geometry of the complexes. Energy-dispersive X-ray analyses (EDX analysis) of the complexes show the metal content along with C, N, O, and Cl, suggesting the formation of metal complex with the anchored ligand at various sites (Fig. 2). The ratios of metals to other elements obtained from EDX analysis are quite similar to the data obtained from elemental analysis. The presence of the metals can be further proved by energy-dispersive spectroscopy analysis of X-rays (EDAX) (Fig. 2a-d).

IR spectral study

The modes of attachment of metals (Cu, Ni, and Co) onto the support was confirmed by comparison of the FTIR

Table	1	Elemental	analysis
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	C (%)	H (%)	O (%)	N (%)	Cl (%)	Metals (%)
Chloromethylated polystyrene	70.9 (70.82)	6.0 (5.90)	-	-	23.3 (23.27)	-
PS-teta(B)	76.6 (76.49)	6.0 (5.97)	6.4 (6.37)	11.2 (11.15)	_	-
PS-Cu(II)teta	68.2 (68.14)	4.9 (4.96)	5.7 (5.67)	10.0 (9.93)	_	3.1
PS-Ni(II)teta	68.8 (68.73)	5.1 (5.01)	5.8 (5.72)	10.1 (10.02)	_	3.1
PS-Co(II)teta	68.7 (68.70)	5.0 (5.00)	5.8 (5.72)	10.1 (10.01)	-	2.9

Calculated values are given in parentheses

Fig. 1 FE SEM image of polymer-anchored Schiff base ligand (**a**) and polymer-anchored complexes Cat-1, Cat-2, and Cat-3 (**b**, **c**, and **d**)



spectra of the polymers before and after loading with metals, both in the mid-IR $(4,000-400 \text{ cm}^{-1})$ and far-IR $(600-50 \text{ cm}^{-1})$ regions (Table 2). The IR spectrum of pure chloromethylated polystyrene has an absorption band at $1,261 \text{ cm}^{-1}$ due to the C–Cl group, which was absent in the ligand and the catalysts. IR spectra show a stretching vibration for CH₂ at 2,918 cm⁻¹ for the polymer-bound ligand and its complexes. The stretching vibrations of C=N bonds appeared at $1,639 \text{ cm}^{-1}$ for the Schiff base and polymer-bound Schiff base ligand which is lowered to 1,588-1,625 cm⁻¹ in the metal complexes, indicating the coordination of azomethine nitrogen to the metal [23]. A peak at 3,433 cm⁻¹ for secondary amine (NH) group for the Schiff base compound is absent for the polymer-bound Schiff base ligand and metal complexes proving the attachment of polystyrene and homogeneous Schiff base through the N-atom of secondary amine group of triethylenetetramine moiety. Another band at $3,325 \text{ cm}^{-1}$ is noticed for O-H stretching, which is not observed for the metal complexes as the OH group coordinates with metals through oxygen. The peaks of M-O for the metal complexes are observed around 630–680 cm^{-1} [24]. These are different since they are influenced by the metal. In the far-IR data, the bands are due to the M-N stretching vibration around 520–580 cm^{-1} [24], which established the formation of the metal complexes through M-N bonding. Another peak at 1,270 cm⁻¹ due to the C–O bond changed

to 1,298 cm⁻¹ (PS-Cu(II)teta), 1,320 cm⁻¹ (PS-Ni(II)teta), and 1,315 cm⁻¹ (PS-Co(II)teta) confirming the metal oxygen coordination [25, 26].

TGA-DTA studies

Thermal stability of complexes was investigated using TGA-DTA at a heating rate of 10 °C/min in air over a temperature range of 30–500 °C. TGA curves of the polymer-supported metal complexes are shown in Fig. 3. The polymer-anchored ligand decomposed in the temperature range 190–200 °C (data not shown). The polymer-supported Cu(II) Schiff base complex decomposed at 220 °C, but the polymer-supported Co(II) and Ni(II) complexes decomposed at 330 and 240 °C. So from the thermal stability, the polymer-supported metal complexes degraded at significantly high temperature and the polymer-supported Co(II) complex was more stable than other two catalysts.

Electronic spectral studies

The electronic spectra (Fig. 4) of the polymer-supported metal complexes were recorded in diffuse reflectance spectrum mode as $MgCO_3/BaSO_4$ disks due to their solubility limitations in common organic solvents. In the UV spectrum of the ligand, two absorption bands are observed at 265





Compound	Color	IR(cm ⁻¹ , KBr) ^a					
		NH (secondary)	М–О	C=N	M–N	O–H	С–О
Schiff base-teta(A)	Yellow	3,433	_	1,639	_	3,325	1,270
PS-teta(B)	Yellow	-	-	1,639	-	3,325	1,270
PS-Cu(II)teta	Green	-	652	1,588	548	-	1,298
PS-Ni(II)teta	Greenish yellow	-	630	1,625	513	-	1,320
PS-Co(II)teta	Pinkish brown	_	684	1,606	573	-	1,315

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

^a Infrared spectra measured as KBr pellets



Fig. 3 Thermal studies of polymer-anchored complexes Cat-1, Cat-2, and Cat-3

and 348 nm, assigned to the transition $n-\pi^*$ and $\pi-\pi^*$, respectively. The electronic spectrum of the Cat-1 exhibits a band at 425 nm (sh.) that is assigned to d-d transition [27]. The band at 275 nm is presumably caused by charge transfer. Cat-3 shows a band at 442 nm (sh.), which indicates d-d transition [28]. The band at 272 nm is assigned to charge transfer transition. Cat-2 exhibits three bands at 245, 268, and 421 nm (sh.). The first two are due to the charge transfer, and the last one may be assigned to d-d transition [29].

Catalytic activity

Oxidation of styrene

Oxidation of styrene, catalyzed by PS-Cu(II)teta, PS-Ni(II)teta, and PS-Co(II)teta using H_2O_2 as an oxidant, gave styrene oxide and benzaldehyde as chief products, as shown in Scheme 2. Preliminary experiments showed the good activity of PS-Cu(II)teta among these catalysts, it was, therefore, taken as a representative, and the different



Fig. 4 DRS-UV-visible absorption spectra of polymer-anchored Schiff base ligand (a) and polymer-anchored complexes Cat-1, Cat-2, and Cat-3 (b, c, d)

parameters, namely amount of oxidant (moles of H_2O_2 per mole of styrene), amount of catalyst, and temperature were checked to get optimized reaction conditions for the maximum oxidation of styrene.

To determine the best temperature, the oxidation of styrene has been investigated with different temperatures with PS-Cu(II)teta as catalyst. The oxidation reaction was carried out with various reaction temperatures from 40 to 80 °C using 1:2 mmol ratio of styrene to H_2O_2 with acetonitrile as solvent for duration of 8 h, and the results are shown in Fig. 5. The optimum temperature was found to be 60 °C. Lower temperatures do not favor the formation of products because the catalyst is less active. At a higher temperature, the yield and selectivity of product decreases.

Similarly, for three different amounts viz. 0.05, 0.1, and 0.15 mmol of catalyst, under the above reaction conditions, using 0.05 mmol catalyst conversion was only 65%, while using 0.1 and 0.15 mmol catalyst, conversions were maximum at 94 and 93%, respectively. However, at the





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)

expense of H_2O_2 , 0.1 mmol catalyst can be considered sufficient to carry out the reaction.

The oxidation of styrene was examined using different solvents. The selected solvent should possess certain criteria such as it should be stable and it should dissolve the substrate and oxidant. Table 3 shows the influence of solvent on the conversion of styrene and selectivity of styrene oxide using the polymer-supported copper catalyst. The selectivity of styrene oxide is in the order: acetonitrile > H_2O > MeOH > MePh. The results indicate that the epoxidation reaction does not proceed in toluene solvent. The reaction, however, shows low activity and

Table 3 Styrene epoxidation using different solvents with Cat-1

Entry	Solvent	Conversion (%) ^a	Selectivity (%) ^a	
			Styrene oxide	Benzaldehyde
1	Toluene	0	0	0
2	MeOH	20	18	82
3	H_2O	60	65	35
4	ACN	94	90	10

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

^a Determined by GC

epoxidation selectivity in methanol, and the main product is benzaldehyde. For the present reaction, the catalysts exhibit the highest catalytic activity and selectivity for styrene oxide in acetonitrile media, because it is a polar solvent, has high dielectric constant, and dissolves a wide range of chemical compounds.

In this study, the effects of different oxidants like TBHP, H_2O_2 , PhIO, and molecular oxygen over this catalyst were examined in the oxidation reaction of styrene. The results of this study are given in Table 4. The reaction shows almost no conversion when molecular oxygen was used as oxidant. Oxidants like molecular O_2 and PhIO are clearly less efficient than TBHP and H_2O_2 as is evident from the percentage of conversion of styrene. TBHP and H_2O_2 proved to be the best among the three oxidants used in these catalytic oxidation reactions, but in the present study we chose H_2O_2 for environmentally benign reaction condition.

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

Entry	Oxidant	Conversion	Selectivity (%) ^a			
		(%)"	Styrene oxide	Benzaldehyde		
1	None	0	0	0		
2	PhIO	15	75	25		
3	O ₂ (1 atm)	32	70	30		
4	TBHP	92	89	11		
5	H_2O_2	94	90	10		

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

^a Determined by GC



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

For three different styrene to aqueous 30% H₂O₂ molar ratios, viz. 1:1, 1:2, and 1:3, the amount of styrene (10 mmol) and catalyst (0.1 mmol) was taken in acetonitrile (10 mL), and the reaction was carried out at 60 °C. The formation of products was regularly analyzed at time intervals. As illustrated in Fig. 6, the conversion of styrene improved from 52 to 94% upon increasing the styrene to aqueous 30% H₂O₂ molar ratio from 1:1 to 1:2, though selectivity in 1:1 condition is high. The oxidation remained nearly constant upon further increasing this ratio to 1:3, which suggested that a large amount of oxidant is not an essential condition to improve the oxidation of styrene.

Thus, for the maximum oxidation of 10 mmol of styrene, other optimized parameters were catalyst (0.1 mmol), H_2O_2 (20 mmol), acetonitrile (10 mL), and reaction temperature (60 °C). PS-Co(II)teta and PS-Ni(II)teta, were also tested under the above optimized reaction conditions, and the results are presented in Tables 5 and 6. It is clear from the data that PS-Cu(II)teta exhibits better catalytic activity with 94% conversion, followed by PS-Co(II)teta with 88%. Catalyst PS-Ni(II)teta has shown only 80% conversion after 8 h of reaction time.

Oxidation of other substrates with the Cat-1

In order to explore further the catalytic activity and selectivity of the cat-1, oxidation of other olefins, alkanes, alcohols, and thioethers was investigated under the optimized reaction conditions with some excellent results (Table 5). Cyclic olefins such as cyclohexene and cyclo-octene are oxidized with high yields. The results showed that the conversion is 54% with 94% epoxide selectivity in the case of cyclooctene, while the oxidation of cyclohexene is with 85% conversion and 70% epoxide selectivity with allylic oxidation products cyclohexene-1-one and cyclohexene-1-ol in small extent.

It is clear from Table 5 that the selectivity of the different oxidation products formed varies in the order: epoxide > aldehyde for the olefins, while ethylbenzene gave acetophenone with 65% of selectivity and toluene formed benzaldehyde in 100% selectivity. Benzyl alcohols gave the corresponding aldehyde with maximum selectivity also. The thioethers gave the corresponding sulfoxides in 100% selectivity. Moreover, the conversion % and the turnover frequency (TOF) are high in most of the reactions.

Oxidation using Cat-2, Cat-3

In search of the activity of other two catalysts (Cat-2 and 3), the oxidation reaction of styrene, cyclohexene, benzyl alcohol, and ethyl benzene was done under the same optimized reaction conditions as for cat-1 (Table 6). Cat-2 and 3 are less active than Cat-1. Cat-2 gave styrene oxide with 84% selectivity in 80% total conversion, while Cat-3 gave epoxide with 92% selectivity in 88% conversion. For the cyclohexene oxidation, Cat-3 proved superior than Cat-2 with 80% conversion and 69% selectivity for epoxide. For the benzyl alcohol and ethylbenzene oxidation, Cat-3 gave better results over Cat-2 with 98 and 62% conversion, respectively, with high selectivity for benzaldehyde and acetophenone in that order. It is to be noticed that the order of selectivities of the products using all Catalysts Cat-1, 2, and 3 are in same array for the oxidation of styrene, cyclohexene, benzyl alcohol, and ethylbenzene, etc. with H₂O₂. Other catalysts from the literature are also compared with our catalysts in Table 6 [15, 30–33].

Table 5	Oxidation	of	different	substrates	using	Cat-1

Entry	Substrate	Conversion (%) ^a	TOF (h^{-1})	Selectivity of the product (%) ^a			
	Olefins			Epoxide	Aldehyde/ketone	Alcohol	
1	Styrene	94	83.93	90	10	_	
2	Cyclohexene	85	75.89	70	22	8	
3	Cyclooctene	54	48.21	94		6	
5	α-Pinene	90	80.35	63	12	15	
6	Limonene	92	82.16	65	12	13	
	Alkanes			Aldehyde	Ketone		
7	Ethylbenzene	90	80.35	35	65		
8	Toluene	35	31.25	100	-		
	Alcohols			Aldehyde	Ketone	Carboxylic acid	
9	Benzyl alcohol	100	89.30	88	-	12	
10	4-Methyl benzyl alcohol	95	84.83	86	-	14	
11	4-Nitro benzyl alcohol	90	80.35	80	-	20	
12	1-Phenyl ethanol	97	86.62	-	100	-	
	Thioethers			Sulfoxide			
13	Phenyl sulfide	90	80.35	100			
14	Methyl phenyl sulfide	87	77.69	100			

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

^b Determined by GC

Heterogeneity test

To determine whether the catalyst is actually functioning in a heterogeneous manner, a hot-filtration test was performed in 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. The gas chromatographic analysis showed no increment in the conversion. Atomic absorption spectrometric analysis of the filtrate confirmed that no metals were present in the reaction mixture. Metal content of the recycled catalysts also remained unaltered indicating no leaching of the metal from the polymer support. These results confirm that no leaching of the metal from the catalyst takes place during catalytic reaction.

Catalyst recycles

The stability of PS-M(II)teta complexes was studied in repeated styrene oxidation reactions. The catalysts were separated from the reaction mixture after each experiment by filtration, washed with methanol, and dried carefully before reuse in the subsequent run. After the use of catalyst for five consecutive times, the styrene conversion was 85%. The nature of the recovered catalyst has been followed by IR and UV–vis spectra. The results indicated that the catalyst after reusing several times showed no change in its IR and UV–vis spectra. These observations show that PS-M(II)teta complexes remain intact after the first oxidation cycle. The results are presented in Table 7.

Conclusion

Polymer-anchored Schiff base complexes of copper(II), nickel(II), and cobalt(II) have been synthesized and characterized by different spectrophotometric methods. The catalytic activities of these complexes were tested for the liquid-phase oxidation of olefins using hydrogen peroxide as the oxidant. Excellent yield and selectivity of these catalysts toward the oxidation of olefins were observed. The complexes are also effective for the oxidation of other organic substrates like aromatic alcohols, alkanes, and thioethers. These polymer-anchored catalysts are easy to build, air-stable, inexpensive, and nonpolluting solids. The

- ···· J · ···	Conversion (%)	Selectivity of	Reference		
			СНО		
Cat-1 Cat-2 Cat-3 PS-[Cu(ligand) _n] PS-K[VO(O_2) ₂ (2-pybmz)]	94 80 88 57 73.2	90 84 92 3.6 2.9	10 26 8 63.7 65.7 0	он 	This work This work This work 30 15
Cat-1 Cat-2 Cat-3 PS-[Cu(ligand) _n] Cu(II)-Cyclam-SBA-16	85 76 80 51 77.8	70 68 69 2.8 1.3 0	22 20 21 12.9 7.3 CHO	8 12 10 83.3 13.7	This work This work This work 30 31
Cat-1 Cat-2 Cat-3 PS-[Cu(hmbmz) ₂] PS-[Cu(ligand) _n]	90 58 62 60.8 15	65 64 65 66.6 4.5	35 36 35 33.4 70.5		This work This work This work 32 30
Cat-1 Cat-2 Cat-3	100 96 98	CHO 88 85 87	соон 12 15 13		This work This work This work
	Cat-1 Cat-2 Cat-3 PS-[Cu(ligand) _n] PS-K[VO(O_2) ₂ (2-pybmz)] Cat-1 Cat-2 Cat-3 PS-[Cu(ligand) _n] Cu(II)-Cyclam-SBA-16 Cat-1 Cat-2 Cat-3 PS-[Cu(ligand) _n] PS-[Cu(ligand) _n] PS-[Cu(ligand) _n]	Cat-194Cat-280Cat-388PS-[Cu(ligand)_n]57PS-K[VO(O_2)_2 (2-pybmz)]73.2Cat-185Cat-276Cat-380PS-[Cu(ligand)_n]51Cu(II)-Cyclam-SBA-1677.8Cat-190Cat-258Cat-362PS-[Cu(ligand)_n]15Cat-190Cat-258Cat-362PS-[Cu(ligand)_n]15Cat-1100Cat-296Cat-398PyC493.6	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

Table 6 A comparison of polymer-anchored complex catalysts Cat-1, 2, and 3

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

^b Determined by GC

catalysts were found to exhibit higher catalytic activity compared with the corresponding neat complexes. The remarkable advantages with the use of the catalysts are the ready accessibility of the catalysts, their reusability, and storage. The catalysts can withstand more stringent reaction conditions and can be recycled several times with no appreciable loss of catalytic activities. Easy product recovery and recycling efficiency along with high selectivity of these catalysts may be useful for the synthesis of different fine chemicals under eco-friendly conditions.

 Table 7 Recycling efficiency of the catalysts for the oxidation of styrene

Recycle	Conversion (%) ^b						
	Cat-1	Cat-2	Cat-3				
1	94	90	92				
2	93	89	92				
3	92	87	92				
4	90	86	91				
5	90	85	90				

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

^b Determined by GC

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