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Synthesis, characterization, and catalytic activity of a polymer-supported copper(II) complex with a thiosemicarbazone ligand

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Abstract A thiosemicarbazone Cu(II) complex anchored to a polystyrene framework has been synthesized and characterized by analytical and spectroscopic techniques. The complex was found to be a highly active catalyst for the oxidation of various organic substrates including alkenes and alcohols using H_2O_2 as oxidant. The reaction conditions were optimized with respect to temperature, solvent, oxidant, catalyst amount, and substrate to peroxide ratio. The heterogeneous catalyst was reused five times without significant loss of activity. A comparison between the catalytic activities of this polymer-supported Cu(II) complex and its homogeneous analogue was carried out.

Introduction

The oxidation of alkenes to oxygen-containing value-added products like alcohols, aldehydes, ketones, acids, epoxides, etc. is an extremely important reaction in both chemical and pharmaceutical industries [1–3]. Similarly, the oxidation of primary and secondary alcohols to carbonyl compounds is one of the simplest and most useful 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].

In homogeneous catalysis, excellent catalytic efficiencies are obtained for the oxidation of alkenes [6–8] under liquid-phase conditions where the catalyst, substrate, oxidant, and product(s) are in a single phase with the solvent. Despite the remarkable utility of homogeneous catalysts in organic synthesis, they suffer from a significant drawback in that they often remain as contaminants in the organic products at the end of the reaction. Another problem with homogeneous catalysts is related to catalyst recovery and/or reuse, affecting the overall economics of the process [9, 10]. In the recent past, there has been an increasing interest in the development of greener catalytic processes, which are also economically viable. Immobilization of the catalyst on an insoluble support is a useful approach because this enhances the thermal stability, selectivity, recyclability, and easy separation of the expensive catalyst from the reaction products [11, 12]. Many effective and recyclable heterogeneous catalysts have been studied for liquid-phase oxidations [13, 14]. Various approaches have been focused on the incorporation of metal-based catalysts onto or into inert supports, such as, alumina [15], amorphous silicates [16], polymers [17], zeolites [18], and MCM-41 [19]. Application of polymer-supported complexes in catalytic reactions has received much attention in recent years [20–23]. Chloromethylated polystyrene cross-linked with divinylbenzene is one of the most widely employed macromolecular supports for immobilization of homogeneous catalysts [24]. These polymer-supported complexes have received considerable attention due to their potential advantages over homogeneous analogues.

In the present study, our initial efforts have focused on developing a ‘green’ catalytic oxidation system that employs hydrogen peroxide, an environmentally friendly

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oxidant whose only oxidation by-product is water [25]. Hydrogen peroxide is a very attractive oxidant due to ready availability, high oxygen content, and ease of use. Here, we have developed a polymer-supported [PS-Cu-TSC] catalyst, and catalytic performances are investigated in the liquid-phase allylic oxidation of various alkenes and alcohols using 30% H_2O_2 as oxidant in acetonitrile medium. The effects of different experimental parameters were investigated in order to optimize the reaction conditions. We have also compared the catalytic activity of the polymer-supported catalyst with its homogeneous analogues.

Experimental

Analytical-grade reagents and freshly distilled solvents were used throughout. Liquid substrates were predistilled and dried using the appropriate molecular sieve. Distillation and purification of the solvents and substrates were done by standard procedures [26]. Chloromethylated poly(styrene-divinyl benzene) and aromatic alcohols were supplied by Sigma–Aldrich. Other reagents were procured from Merck and used without further purification.

Morphologies of the polymer-anchored ligand and [PS-Cu-TSC] catalyst were analyzed using a Jeol JSM 6700 scanning electron microscope. The thermal stability of the polymer-supported ligand and [PS-Cu-TSC] catalyst was determined using a Mettler Toledo TGA/SDTA 851 instrument. FTIR spectra were recorded on a Perkin-Elmer FTIR 783 spectrophotometer using KBr pellets. Diffuse reflectance UV–Vis spectra were taken using a Shimadzu UV-2401PC double-beam spectrophotometer having an integrating sphere attachment for solid samples. ^1H NMR spectra were recorded at 400 MHz using a Bruker DPX-400 spectrometer. Copper content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS).

General procedure for catalytic oxidation reactions

The oxidation reactions were carried out in a round-bottom flask fitted with a water condenser and placed in an oil bath with vigorous stirring. Substrate (5 mmol) was taken in acetonitrile (10 mL) for different sets of reactions together with 0.05 g catalyst in which 10 mmol of H_2O_2 (30% in aq.) was added. When the reaction was carried out under O_2 atmosphere, O_2 gas was purged into the flask continuously. Aliquots of the reaction mixture were withdrawn at regular intervals and analyzed with a Varian 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a Flame Ionization Detector. Chlorobenzene was used as an internal standard. All reaction products were identified by using an Agilent GC–MS.

Synthesis of the catalyst

The Schiff base complex (**1**) was prepared by condensing a solution of 5-nitrosalicyl-aldehyde (10 mmol, 1.671 g) in ethanol (25 mL) with an aqueous ethanolic solution of thiosemicarbazide (10 mmol, 0.911 g). The reaction mixture was refluxed for 5 h in a water bath. After completion of the reaction, the resulting mixture was poured onto crushed ice whereby a precipitate was obtained. The precipitate of (**1**) was filtered off, washed several times with water, recrystallized from ethanol, and finally dried. The Schiff base complex (**1**) (1.05 g) was dissolved in DMF (15 mL) and reduced using Pd/C at room temperature and one atmosphere pressure of H_2 for 24 h. The obtained red solution (**2**) was filtered. To the filtrate, chloromethylated polystyrene (5 mmol, 0.90 g) was added, and the reaction mixture was stirred and refluxed for 12 h. After completion of the reaction, the polymer-supported ligand (**3**) was separated by filtration and dried in a vacuum oven. Next, the polymer-supported ligand (**3**) (1 g) was suspended in methanol (20 mL). A solution of $CuCl_2$ (0.6 mmol, 0.1 g) in methanol (5 mL) was added with constant stirring; then, the suspension was refluxed for 24 h. After cooling to room temperature, the yellow polymer-supported [PS-Cu-TSC] catalyst was filtered out, washed thoroughly with methanol, and dried under vacuum. The outline for the preparation of the polymer-supported Cu(II) Schiff base complex is given in Scheme 1.

Results and discussion

Characterization of the polymer-supported complex

Due to the insolubility of the polymer-supported [PS-Cu-TSC] complex in all common organic solvents, characterization was limited to its physicochemical properties, SEM, TGA, IR, and UV–Vis spectral data. The structures of ligands were established by ^1H NMR spectroscopy.

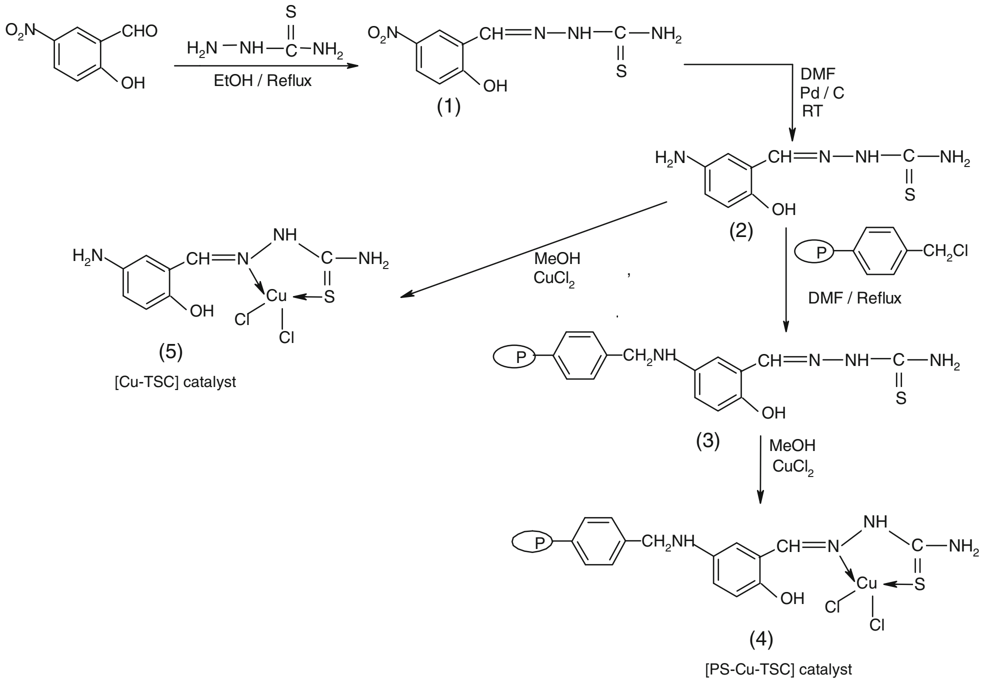
^1H NMR (DMSO-d_6) (Ligand 1): δ 11.55 (s, 1H), 9.85 (s, 1H), 8.37 (s, 1H), 8.07 (s, 2H), 7.32 (s, 1H), 6.84 (d, 1H), 6.66 (d, 1H).

^1H NMR (DMSO-d_6) (Ligand 2): 11.26 (s, 1H), 9.85 (s, 1H), 8.36 (S, 1H), 8.08 (s, 2H), 7.30 (s, 1H), 8.10 (s, 2H), 6.80 (d, 1H), 6.65 (d, 1H).

Chemical analysis suggests 1.69 wt% Cu in the immobilized Cu(II) catalyst.

Field emission scanning electron micrographs for single beads of the polymer-supported thiosemicarbazone ligand and its copper complex were recorded to understand the morphological changes occurring on the polystyrene beads at various stages of the synthesis. Figure 1 shows the SEM

Scheme 1 Synthesis of the polymer-supported Cu(II) Schiff base complex



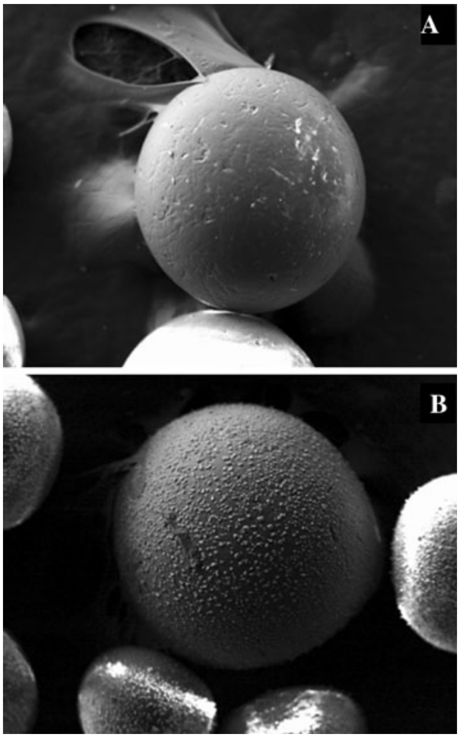


Fig. 1 SEM image of polymer-supported ligand (**a**) and polymer-supported [PS-Cu-TSC] catalyst (**b**)

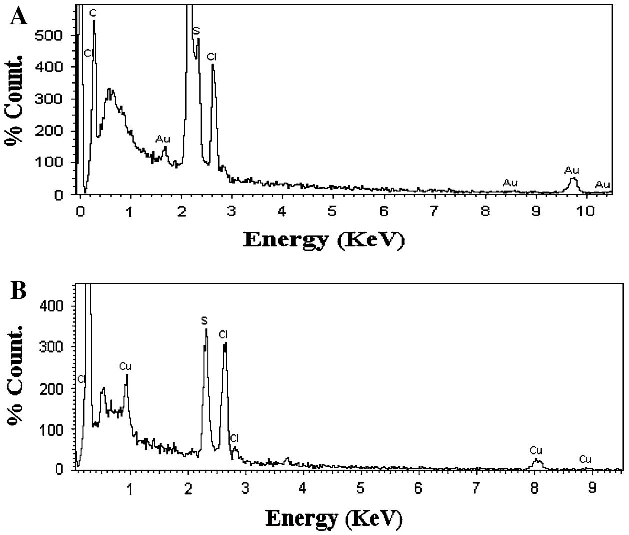


Fig. 2 EDX spectra of polymer-supported ligand (**a**) and polymer-supported [PS-Cu-TSC] catalyst (**b**)

image of the polymer-supported thiosemicarbazone ligand and the immobilized copper complex on functionalized polymer. The pure chloromethylated polystyrene bead has a smooth surface (not shown). Introduction of the ligand into the polystyrene beads through covalent bonding causes light roughening of the top layer of the beads. The image of the metal complex shows further roughening of the surface layer, which may be due to interaction of the metal atom with the ligand to accommodate the fixed geometry of the complex. The presence of copper along with sulfur and chlorine was verified by energy dispersive spectroscopy analysis of X-rays (EDX) (Fig. 2), which is consistent with the formation of the metal complex with the polymer-anchored ligand.

The coordination mode of the ligand was confirmed by IR spectral bands in both the mid (4,000–400 cm^{-1}) and the far (600–50 cm^{-1}) IR regions. For ligand 1, the $-NH_2$ and NH groups gave bands at 3,420 and 3,216 cm^{-1}, respectively. In addition, a strong band at 1,535 cm^{-1} was assigned to ν-NO_2. The bands due to $\nu(C = S)$ and $\nu(C = N)$ appeared at 1,030 and 1,570 cm^{-1}. In ligand 2, the reduction of the nitro group to the corresponding amine is confirmed by the absence of a peak at 1,535 cm^{-1}. On complexation with copper, the $\nu(C = S)$ and $\nu(C = N)$ bands were shifted toward lower frequency at 1,021 and 1,545 cm^{-1}. This suggests that the ligand chelates through its N (azomethine) and S atoms. In complex 5, [Cu-TSC], bands at 412, 320 and 306 cm^{-1} were assigned to ν(Cu–N) [27], ν(Cu–S) [28], and ν(Cu-Cl) [29], respectively.

The FTIR spectra of the polymer-supported Schiff base ligand and polymer-supported complex were also studied. The intensity of the spectrum of the polymer-supported complex was weak due to the low concentration of the complex. The IR spectrum of the supported complex is, however, very similar to that of the free complex. The IR spectrum of the polymer-supported thiosemicarbazone ligand was compared with the polymer-supported [PS-Cu-TSC] catalyst in order to confirm the coordination of the metal atom with the thiosemicarbazones ligand. The existence of a strong band at 1,028 cm^{-1} due to $\nu(C = S)$ and absence of any band in the region 2,500–2,600 cm^{-1} from ν(C-SH) suggested that the thiosemicarbazone remains in its thione form. The polymer-anchored thiosemicarbazone ligand exhibited a strong band at 1,565–1,578 cm^{-1}, which may be assigned to the $\nu(C = N)$ stretch of the azomethine linkage. In the copper complex, this band was shifted to lower frequency by 32 cm^{-1} and this was attributed to the coordination of azomethine nitrogen to the metal with formation of an M–N band. The $\nu(C = S)$ band was shifted to lower frequency by 14 cm^{-1} for the complex, indicating the bonding of thionic sulfur to the metal. The spectrum of the ligand exhibited a broad band in the 3,245–3,360 cm^{-1} region, which may be due to ν(O–H) and ν(N–H). These bands remain at almost the same positions in the [PS-Cu-TSC] catalyst, suggesting that the terminal amino group was not involved in coordination [30]. More information on the coordination of the polymer-supported ligand to the central metal comes from the far IR data. New bands at 409 cm^{-1} for $\nu(\text{Cu-N}_{\text{azomethine}})$, 324 cm^{-1} for ν(Cu–S), and 304 cm^{-1} for ν(Cu–Cl) were present in the spectrum of the [PS-Cu-TSC] catalyst.

The electronic spectrum of the polymer-supported complex was recorded in diffuse reflectance mode as a $BaSO_4$ disk, due to the solubility limitations. The UV–Vis spectra (DRS) are shown in Fig. 3. The UV spectrum for the catalyst exhibits three bands at ca. 420–440, 260–300, and 330–360 nm. The first band is assumed to be due to the $2B_{1g} \rightarrow 2A_{1g}$ transition, and the other two are probably due to charge transfer transitions. From the spectroscopic data, a distorted tetrahedral geometry may be assigned to the [PS-Cu-TSC] catalyst [31].

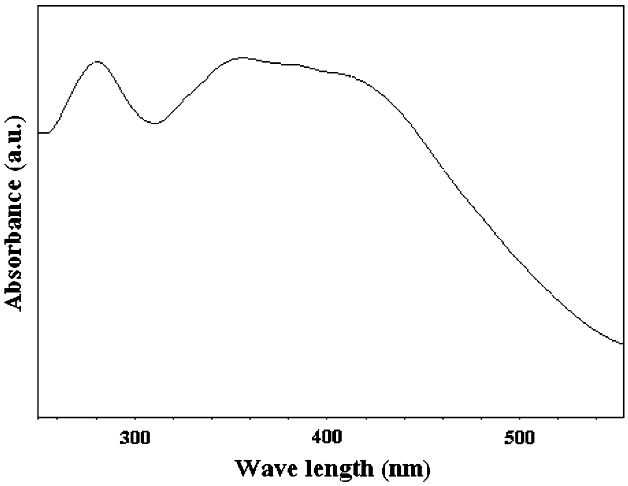


Fig. 3 Electronic spectra of polymer-supported [PS-Cu-TSC] catalyst

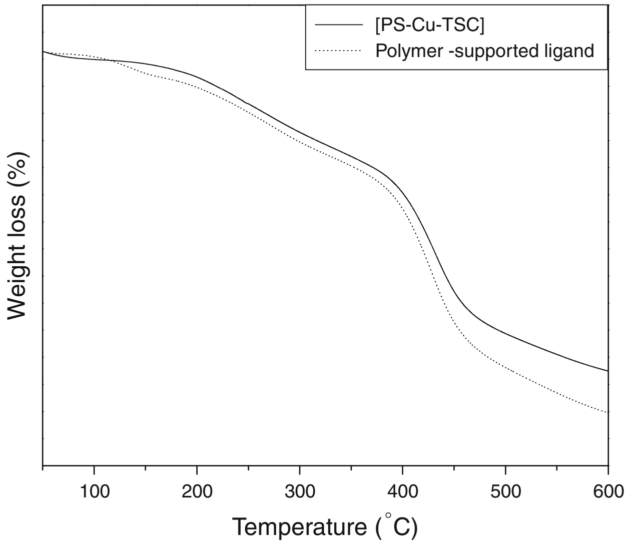


Fig. 4 Thermogravimetric weight loss plots for polymer-supported ligand (**a**) and polymer-supported [PS-Cu-TSC] catalyst (**b**)

Thermogravimetric analysis of the polymer-bound complex was performed in air at a heating rate of 10 °C min^{-1}. The TG-data are depicted in Fig. 4. The polymer-supported ligand decomposed at 380 °C, while the polymer-supported [PS-Cu-TSC] catalyst degraded at the slightly higher temperature of 400 °C.

Catalytic activity

We explored the catalytic activity of our polymer-anchored complex toward oxidation reactions, starting with styrene as a model substrate. The effects of solvent, oxidant, temperature, time, catalyst amount, and substrate to oxidant ratio on the oxidation reaction were first surveyed. Benzaldehyde was identified as the major product of this reaction, with a small amount of styrene oxide.

At first we investigated the effects of different solvents (both polar and non-polar). The results are summarized in Table 1. The optimum catalytic activity was observed in acetonitrile (Table 1, entry 1). In methanol and dichloromethane, moderate conversion was obtained. No catalytic activity was observed when a non-polar solvent, namely toluene, was employed. The high catalytic activity in acetonitrile may be due to the polarity as well as high dielectric constant of the solvent and better solubility of the substrate and oxidant in the solvent.

The effect of oxidant on the reaction was also important because the desired products were not obtained in any noticeable amounts in the absence of oxidant (Table 1, entry 6). The ability of different oxidants, such as H_2O_2, TBHP, NaOCl, PhIO, and mol. O_2, in the oxidation reaction was studied (Table 1, entry 1–5). When NaOCl or O_2 was used as oxygen source, low conversion of styrene was obtained. TBHP and H_2O_2 were found to be the best oxygen sources. Considering the green point of view, H_2O_2 was used as the oxidant for further studies.

The reaction temperature has a very strong influence in these oxidation reactions. No product formation was observed at room temperature. As the temperature was increased from 30 to 60 °C, the conversion of styrene increased. The reaction performed at 60 °C appeared provided the highest yield of product.

Table 1 Oxidation of styrene using different oxidants, solvents, and catalyst amounts catalyzed by [PS-Cu-TSC] complex

Entry	Solvent	Oxidant	Catalyst amount (g)	Conversion (%)[a]
1	**CH_3CN**	**H_2O_2**	**0.05**	**81**
2	CH_3CN	TBHP	0.05	80
3	CH_3CN	NaOCl	0.05	37
4	CH_3CN	Mol. O_2	0.05	22
5	CH_3CN	PhIO	0.05	41
6	CH_3CN	–	0.05	0
7	CH_3OH	H_2O_2	0.05	45
8	H_2O	H_2O_2	0.05	34
9	DCM	H_2O_2	0.05	19
10	Toluene	H_2O_2	0.05	0
11	CH_3CN	H_2O_2	–	2
12	CH_3CN	H_2O_2	0.025	49
13	CH_3CN	H_2O_2	0.10	81

Reaction conditions: styrene (5 mmol), oxidant (10 mmol), solvent (10 mL), temperature (60 °C), and time (6 h)

[a] Determined by GC

A control experiment showed that the reaction did not occur in the absence of catalyst (Table 1, entry 11). In order to optimize the catalyst amount, different amounts of catalyst were used in the oxidation of styrene. The best results were obtained with 0.05 g Cu catalyst (Table 1, entry 1).

The activity of the polymer-anchored catalyst was also evaluated using three different molar ratios of styrene to H_2O_2. The conversion of styrene was 49, 81, and 81% for styrene to H_2O_2 ratios of 1:1, 1:2, and 1:3, respectively. Hence, 1:2 ratio of styrene to H_2O_2 is sufficient for the good conversion of styrene.

Thus, the optimal parameters for the oxidation of styrene were follows: cyclohexene (5 mmol), 30% H_2O_2 (10 mmol), acetonitrile (10 mL), catalyst (0.05 g), and a reaction temperature of 60 °C. Under these optimum reaction conditions, the oxidation reactions were carried with different alkenes and alcohols. The [PS-Cu-TSC] catalyst efficiently converts a range of alkenes to their corresponding allylic products with H_2O_2 as an oxidant. The results are summarized in Table 2. In the oxidation of cyclohexene, allylic products 2-cyclohexene-1-one and 2-cyclohexene-1-ol were produced (Table 2, entry 5). Styrene was converted to benzaldehyde in high yield (Table 2, entry 1). Substituted styrenes produced selectively the corresponding aldehydes (Table 2, entries 3, 4). Acetophenone was detected in the oxidation of α-methyl styrene as major product (Table 2, entry 2). Trans-stilbene was also oxidized in high yields (Table 2, entry 7), giving benzaldehyde as major product with small amount of benzophenone. This catalytic system showed a good activity in the case of limonene and α-pinene. Limonene was oxidized to carvone and carvenol with other coproducts (Table 2, entry 8). In the oxidation of α-pinene, the major products were verbenone and verbenol (Table 2, entry 9).

Selective oxidation of aromatic alcohols to aldehydes was investigated with the [PS-Cu-TSC] catalyst using the same conditions, as for styrene. As shown in Table 3, benzyl alcohol was oxidized selectively into benzaldehyde (entry 1). The catalyst also showed good activity toward the oxidation of other benzyl alcohols containing substituents such as methyl, methoxy, chloro, and nitro groups (Table 3, entries 2–5). Electron-donating or withdrawing substituents on the benzyl alcohols did not affect the efficiency of the oxidation. In all the above cases, trace amount of acids was observed.

Comparison of homogeneous and heterogeneous catalysts

We have also compared the catalytic activity of the present polymer-anchored [PS-Cu-TSC] with its homogeneous

Table 2 Oxidation of alkenes with [PS-Cu-TSC] catalyst

Entry	Substrate	Time (h)	Conversion[a] (%)	Product[b] (selectivity, %)	TOF (h^{-1})
1	Styrene	6	81	Benzaldehyde (93) Styrene oxide (7)	508
2	α-methylstyrene	8	74	Acetophenone (100)	348
3	4-chlorostyrene	6	78	4-chloro benzaldehyde (87) 4-Chlorostyrene epoxide (13)	489
4	4-nitrostyrene	6	80	4-nitro benzaldehyde (88) 4-nitro styrene oxide (12)	501
5	Cyclohexene	6	85	2-cyclohexene-1-one (78) 2-cyclohexene-1-ol (15) Cyclohexene epoxide (7)	533
6	Cyclooctene	8	69	2-cyclooctene-1-one (74) 2-cyclooctene-1-ol (26)	324
7	Trans-stilbene	8	74	Benzaldehyde (83) Benzophenone (12) *trans*-Stilbene oxide (5)	348
8	Limonene	8	54	Carvenone (75) Carvenol (18) Limonene oxide (1,2) (7)	254
9	α-pinene	8	57	Verbenone (69) Verbenol (22) α-pinene oxide (9)	268

Reaction conditions: alkene (5 mmol), 30% H_2O_2 (10 mmol), CH_3CN (10 mL), and temperature (60 °C)

[a] Determined by GC

[b] Products were identified by GC and GC–MS analysis

Table 3 Oxidation of aromatic alcohols with [PS-Cu-TSC] catalyst

Entry	Substrate	Time (h)	Conversion[a] (%)	Product[b] (selectivity, %)	TOF (h^{-1})
1	Benzyl alcohol	6	94	Benzaldehyde (97) Benzoic acid (3)	589
2	4-methyl benzyl alcohol	8	85	4-methyl benzaldehyde (89) 4-methyl benzoic acid (11)	399
3	4-methoxy benzyl alcohol	8	87	4-methoxy benzaldehyde (84) 4- methoxy benzoic acid (16)	409
4	4-chloro benzyl alcohol	10	78	4-chloro benzaldehyde (79) 4- chloro benzoic acid (21)	293
5	4-nitro benzyl alcohol	8	89	4-nitro benzaldehyde (90) 4-nitro benzoic acid (10)	418

Reaction conditions: alcohol (5 mmol), 30% H_2O_2 (10 mmol), CH_3CN (10 mL), and temperature (60 °C)

[a] Determined by GC

[b] Products were identified by GC and GC–MS analysis

analogue [Cu-TSC]. The activity of the homogeneous complex was examined toward oxidation of styrene and benzyl alcohol using same reaction conditions as for the heterogeneous catalyst. The results are summarized in Table 4. The results showed that in the oxidation of styrene and benzyl alcohol, the turnover frequencies (TOF) for the homogeneous catalyst were higher than for the heterogeneous catalyst. Although styrene conversions in heterogeneous systems are comparable with the homogeneous results, the heterogeneous systems showed higher selectivity to benzaldehyde. Additionally, the supported catalyst is expected to have several advantages over the

Table 4 Oxidation of styrene and benzylalcohol with H_2O_2 catalyzed by [Cu-TSC] and [PS-Cu-TSC]

Substrate	Product (s)	Heterogeneous [PS-Cu-TSC]			Homogeneous [Cu-TSC]		
		Time	Conversion (%)	Selectivity (%)	Time	Conversion (%)	Selectivity (%)
Styrene	Benzaldehyde	6	81	93	6	83	85
	Styrene oxide			7			15
Benzylalcohol	Benzaldehyde	8	94	97	8	95	81
	Benzoic acid			3			19

Table 5 Comparison of catalytic activity of styrene oxidation with polymer-anchored [PS-Cu-TSC] complex catalyst and other catalyst reported in literature

Catalyst	Oxidant	Temp (°C)	Reaction time (h)	Conversion (%)[a]	Reference
[PS-Cu-TSC]	H_2O_2	60	8	81	Present
Vit-B_{12}/MCM-41	TBHP	70	8	60	33
PS-[Cu(Ligand)$_n$]	H_2O_2	80	6	57	34
FePcS/NH_2-MCM-48	TBHP	RT	24	65.5	35

[a] Conversion obtained from GC analysis

homogenous one. The polymer-based catalysts can withstand more drastic conditions. The greatest disadvantage of homogeneous [Cu-TSC] is the catalyst degradation in the presence of oxidant, whereas the heterogenized catalyst can be reused several times without significant loss of activity.

Table 5 provides a comparison of the results obtained for our present catalytic system with those reported in the literature [32–34]. The present catalyst exhibited higher conversions compared to the other reported systems.

Heterogeneity tests

A hot filtration test was performed in the oxidation of styrene. During the catalytic reaction, the solid catalyst was separated from the reaction mixture by filtration after 4 h and the determined conversion was 52%. The reaction was then continued out for a further 2 h. The gas chromatographic analysis showed no increase in the conversion. This confirms that the reaction did not proceed upon the removal of the solid catalyst. Atomic absorption spectrometric analysis of the reaction mixtures collected by filtration confirms that Cu is absent from the reaction mixture. These results suggest that the Cu is not being leached out from the catalyst during these catalytic reactions.

Recycling of the catalyst

One of the main reasons of supporting a complex on the polymer is to enhance the life of the resulting catalyst. The reusability of the present catalyst was checked in sequential oxidation of styrene. After the first run, the catalyst was separated by filtration, washed thoroughly, dried under vacuum, and then subjected to another run under the same reaction conditions. The catalyst was reused up to five times in this way, without significant loss of activity. Thus, the yields of the five consecutive runs were 81, 81, 79, 79, and 78%. The IR spectrum of the recycled catalyst was quite similar to that of a fresh sample, indicating the heterogeneous nature of this complex. The analysis of the recovered catalyst by atomic absorption spectroscopy showed no reduction in the amount of copper. The results indicate that this complex is stable under reuse.

Conclusion

In conclusion, we have demonstrated the effectiveness of a polymer-supported copper catalyst for liquid-phase oxidations with the environmentally friendly H_2O_2 as sole oxidant. The [PS-Cu-TSC] catalyst exhibits good activity in the oxidation of various alkenes and alcohols to give selectively the allylic oxidation products. The main advantages of this catalyst are that the synthesis is very simple, the catalytic reactions can be conveniently carried out in air, and the separation of this heterogeneous catalyst can be achieved easily by filtration. The catalyst can be recycled five times without much loss in its activity.

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