



## Synthesis, catalytic oxidation and antimicrobial activity of copper(II) Schiff base complex

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### ABSTRACT

A new polymer supported Cu(II) Schiff base complex was synthesized. The solid complex was characterized by Fourier transform infrared spectroscopy (FT-IR), UV–vis diffuse reflectance spectroscopy (DRS), thermogravimetric analysis (TGA) and scanning electron microscope (SEM). Its homogeneous analogue was also prepared. The catalytic performances of the copper complex in oxidation reactions were evaluated for both homogeneous and heterogeneous systems. The copper(II) complex was found to be efficient catalyst for the oxidation of alkenes, alkanes and aromatic alcohols in the presence of hydrogen peroxide as oxidant at room temperature. The catalytic investigation revealed that the solid complex performs better than the homogeneous one as an oxidation catalyst. The solids containing the immobilized complex can be recovered from the reaction medium and reused almost five times, maintaining good catalytic activity. Furthermore, the in vitro toxicity of the ligand and complex was tested against the growth of bacterial species, viz., *Staphylococcus aureus* and *Escherichia coli*.

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### 1. Introduction

The oxidation of organic compounds with an eco friendly oxidant, aqueous hydrogen peroxide, is a challenging goal of catalytic chemistry [1–3]. In recent years, a considerable amount of research was dedicated to the preparation of various solid heterogeneous copper catalysts and their application for oxidations of various organic compounds [4–8].

Olefin oxidation is especially interesting because of the industrial importance of this type of reaction. Oxidation of alkenes to give oxygen containing value added products like alcohols, aldehydes, ketones, acids, epoxides, etc. is an extremely important and useful reaction in both chemical and pharmaceutical industries [9]. Activation of the carbon–hydrogen bonds of an alkane is considerably more difficult due to its stability. The energy required to overcome this stability leads to deep oxidation rather than selective oxidation [10,11]. On the other hand, the oxidation of primary and secondary alcohols to carbonyl compounds (corresponding aldehydes and ketones) is one of the simplest and most useful transformations in organic chemistry. In particular, the oxidation of benzyl alcohol to benzaldehyde is an important organic transformation which has

applications in the industry of perfumery, pharmaceutical, dyestuff and agrochemicals [12,13].

In the recent past, there has been an increasing interest in developing environmental friendly greener processes which are also economically viable. However, some problems such as excessive use of oxidants, corrosion, difficulty in recovery and separation of the catalyst from reaction mixtures are associated with homogeneous catalysts and make such systems environmentally unsuitable [14]. In recent years, the design and synthesis of catalytically active supported metal complexes have received considerable interest. Many effective and recyclable heterogeneous catalysts have been studied for the liquid phase oxidation [15,16]. Various approaches have been focused on the incorporation of metal-based catalysts onto or into inert supports by different methods, such as alumina [17], amorphous silicates [18], polymers [19], zeolites [20] and MCM-41 [21]. Application of polymer supported catalysts in oxidation reactions has been received attention in recent years due to their potential advantages over the homogeneous one [22–24]. The activity of polymer supported Schiff base complexes of transition metal ions varies with the type of Schiff base ligands, coordination sites and metal ions used in their formation.

In this work, we have prepared homogeneous and its immobilized polymer anchored Cu(II) Schiff base complex. The catalytic efficiency of the neat and polymer supported metal Schiff base complexes was tested in the oxidation of alkenes, alkanes and aro-

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matic alcohols using  $\text{H}_2\text{O}_2$  as oxygen source. Polymer supported copper catalyst showed excellent catalytic activity and selectivity. Comparison of homogeneous and supported catalyst for oxidation reaction was also done. The catalytic activities were also tested with the recycled catalyst. Further, the antibacterial activity of the Schiff base and its copper complex was examined.

## 2. Experimental

### 2.1. Materials

All the reagents used were chemically pure and were of analytical reagent grade. The solvents were dried and distilled before use following the standard procedures [25]. Chloromethylated polystyrene was supplied by Sigma–Aldrich Chemicals Company, USA. Alkenes, alkanes and aromatic alcohols were obtained from Merck or Fluka.

### 2.2. Physical measurements

A Perkin-Elmer 2400C elemental analyzer was used to collect micro analytical data (C, H and N). The copper content of the samples was measured by Varian AA240 atomic absorption spectrophotometer (AAS). The FT-IR spectra of the samples were recorded on a Perkin-Elmer FT-IR 783 spectrophotometer using KBr pellets. Diffuse reflectance spectra (DRS) were registered on a Shimadzu UV/3101 PC spectrophotometer. Magnetic measurement was carried out on a Sherwood Scientific magnetic balance using Gouy method. Mettler Toledo TGA/SDTA 851 instrument was used for the thermogravimetric analysis (TGA). Morphology of functionalized polystyrene and complex were analyzed using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility.

### 2.3. Synthesis of catalyst

The outline for the preparation of homogeneous and polymer supported Cu(II) Schiff base complexes is given in Scheme 1.

#### 2.3.1. Synthesis of 4-acetylpyridine thiosemicarbazone (L)

The Schiff base ligand 4-acetylpyridine thiosemicarbazone was prepared by mixing 4-acetylpyridine and thiosemicarbazide in a stoichiometric ratio [26]. A mixture of 4-acetylpyridine (0.10 mol), thiosemicarbazide (0.10 mol) and methanol (100 ml) was heated under reflux for 2 h after cooling the precipitate was filtered off, washed with methanol, crystallized from methanol to give white crystals.

#### 2.3.2. Synthesis of the $[\text{Cu}(\text{L})(\text{Cl})_2]$ complex

The copper complex  $[\text{Cu}(\text{L})(\text{Cl})_2]$  was prepared by mixing equal volumes (50 ml) of methanol solution of  $\text{CuCl}_2$  (0.170 g, 1.0 mmol) with 4-acetylpyridine thiosemicarbazone solution (0.195 g, 1.0 mmol). The mixtures were refluxed at about  $75^\circ\text{C}$  for 2–3 h on a water bath. On cooling immediately precipitates were settle down and filtered off, washed several times by minimum amount of hot methanol and dried under vacuum over anhydrous  $\text{CaCl}_2$ .

#### 2.3.3. Synthesis of polymer supported Cu(II) Schiff base catalyst $\text{PS}-[\text{Cu}(\text{L})(\text{Cl})_2]$

It was readily prepared in two steps. The chloromethylated polystyrene (2 g) was added to methanolic solution of 4-acetylpyridine thiosemicarbazone (1.07 g in 20 ml) and then refluxed for 24 h. After cooling to room temperature, the light yellow coloured polymer beads were filtered, washed thoroughly with methanol and dried in vacuum. The polymer supported Schiff base

(1 g) was kept in contact with methanol (10 ml) in a round bottom flask. To this, methanolic solution (10 ml) of  $\text{CuCl}_2$  (1%, w/v) was added over a period of 45 min and refluxed for 6 h. Then green coloured copper loaded beads were filtered carefully, washed with methanol and dried in vacuum.

### 2.4. General procedure for oxidation of alkenes, alkanes and aromatic alcohols catalyzed by $\text{PS}-[\text{Cu}(\text{L})(\text{Cl})_2]$

All of the reactions were carried out at room temperature under air in a 25 ml flask equipped with a magnetic stirrer. 30%  $\text{H}_2\text{O}_2$  solution (10 mmol) was added to a mixture of alkene or alkane or aromatic alcohol (5 mmol), catalyst (0.05 g) in  $\text{CH}_3\text{CN}$  (10 ml). After filtration and washing with solvent, the filtrate was concentrated and then analyzed with Varian 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a Flame Ionization Detector. The concentration of products was determined using cyclohexanone as internal standard. All reaction products are identified by using an Agilent GC–MS.

### 2.5. General procedure for oxidation of alkenes, alkanes and aromatic alcohols catalyzed by $[\text{Cu}(\text{L})(\text{Cl})_2]$

To a 25 ml round-bottom flask containing alkene or alkane or aromatic alcohol (5 mmol), neat metal complex ( $1.20 \times 10^{-5}$  mol) in  $\text{CH}_3\text{CN}$  (10 ml) were added a solution of 30%  $\text{H}_2\text{O}_2$  (10 mmol). The resulting mixture was then stirred at room temperature under air, the solvent was evaporated under reduced pressure and the crude was analyzed by GC and GC–MS. The concentrations of products were determined using cyclohexanone as internal standard.

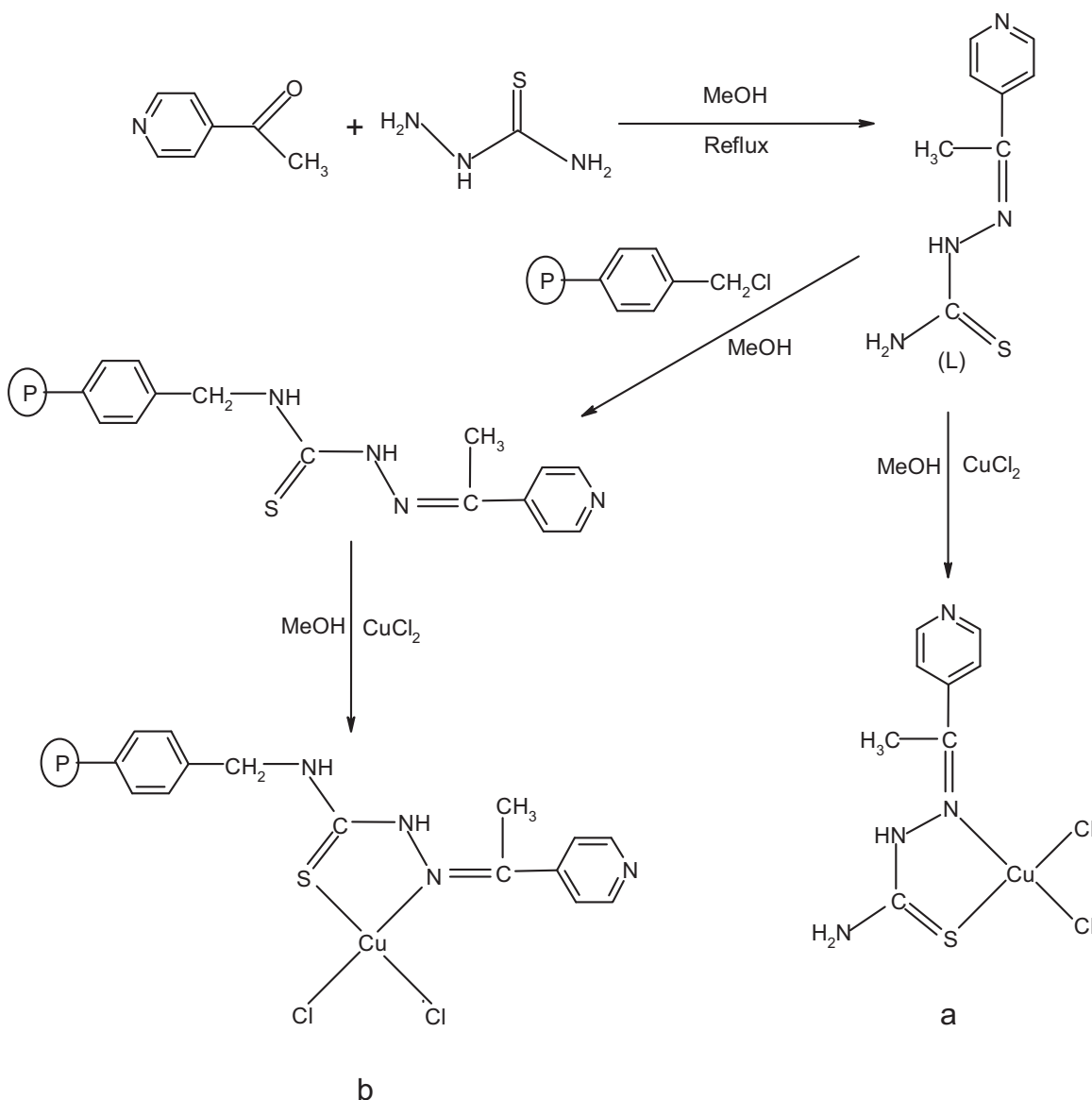
### 2.6. Procedure for antibacterial studies

The nutrient agar medium was prepared by taking 1 l of distilled water in a conical flask followed by the addition of following ingredients one by one (i) beef extract = 10.0 g, (ii) glucose = 1.0 g, (iii) peptone = 10.0 g and (iv) sodium chloride = 5.0 g. The resulting solution was stirred well to get a clear solution. The pH of the solution was adjusted to 7.5. After that, 20.0 g of agar was added to the solution. The above said set up was sterilized at  $120^\circ\text{C}$  for 15 min. A total of 20 ml of the sterilized medium was poured into the sterilized Petri plates and allowed to solidify. The plates were then inoculated with bacterial suspension of *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) through spread plate techniques. Various concentrations (50, 75, 100, 150 ppm) of each compound were made. For each concentration separate Petri plate with preinoculated bacteria was used. On each plate three cups were made and 1 ml of each test compound and Streptomycin were poured on each cup carefully. All the Petri plates were then incubated at  $37 \pm 2^\circ\text{C}$  for 48 h. The diameter (mm) of inhibition zone around each cups were measured separately against each concentration and also against each test bacterium. Streptomycin solution was also treated as reference plate.

## 3. Results and discussion

### 3.1. Characterization of metal Schiff base complex

Due to insolubilities of the polymer supported Cu(II) Schiff base complex in all common organic solvents, its structural investigations were limited to their physicochemical properties, chemical analysis, SEM, TGA, IR and UV–vis spectral data. Table 1 provides the data of elemental analysis, from which it is clear that the obtained values of soluble metal complex are quite comparable with the calculated values. Elemental analysis indicates that the complex is monomeric formed by coordination of 1 mol of metal ion and 1 mol



**Scheme 1.** Synthesis of homogeneous (a) and polymer supported (b) Cu(II) Schiff base complex.

of Schiff base ligand. The metal content of the polymer supported catalyst was estimated by atomic absorption spectrometer and was found to be 2.34%. The chemical composition confirmed the purity and stoichiometry of the neat and polymer supported complexes.

### 3.1.1. Scanning electron micrographs (SEMs) and energy dispersive X-ray analyses (EDAX)

Field emission-scanning electron micrographs for single beads of polymer supported Schiff base ligand and complex were recorded to understand the morphological changes occurred on the polystyrene beads at various stages of the synthesis. In Fig. 1

the SEM image of polymer supported Schiff base ligand (A) and the immobilized copper complex (B) on functionalized polymer are shown. The pure chloromethylated polystyrene bead has a smooth surface (not shown). Introduction of ligands into polystyrene beads through covalent bonding causes the light roughening of the top layer of polymer beads. After metal loading on polymer anchored ligand, changes in morphology of the ligand surface was observed by SEM picture. As expected smooth and flat surface of polymer bead shows slight roughening on complexation. Also presence of copper metal along with sulfur and chlorine can be further proved by energy dispersive spectroscopy analysis of X-rays (EDAX) (Fig. 2)

**Table 1**

Chemical composition and IR stretching frequencies of homogeneous and polymer supported metal Schiff base complexes.

Compound	C (%)	H (%)	N (%)	Cu (%)	$\nu_{\text{C=N}}^{\text{a}}$	$\nu_{\text{M-N}}^{\text{a}}$	$\nu_{\text{M-S}}^{\text{a}}$	$\nu_{\text{M-Cl}}^{\text{a}}$
L: 4-acetylpyridine thiosemicarbazone	49.15 (49.48)	4.97 (5.15)	28.32 (28.86)	-	1635	-	-	-
[CuL(Cl) <sub>2</sub> ]	29.08 (29.22)	2.89 (3.04)	16.95 (17.04)	19.12 (19.33)	1592	530	323	354
PS-L	65.54	5.44	17.93	-	1639	-	-	-
PS-[CuL(Cl) <sub>2</sub> ]	45.68	3.86	12.32	2.34	1615	528	322	353

Calculated values are given in parentheses.

<sup>a</sup> Infrared spectra measured as KBr pellets.

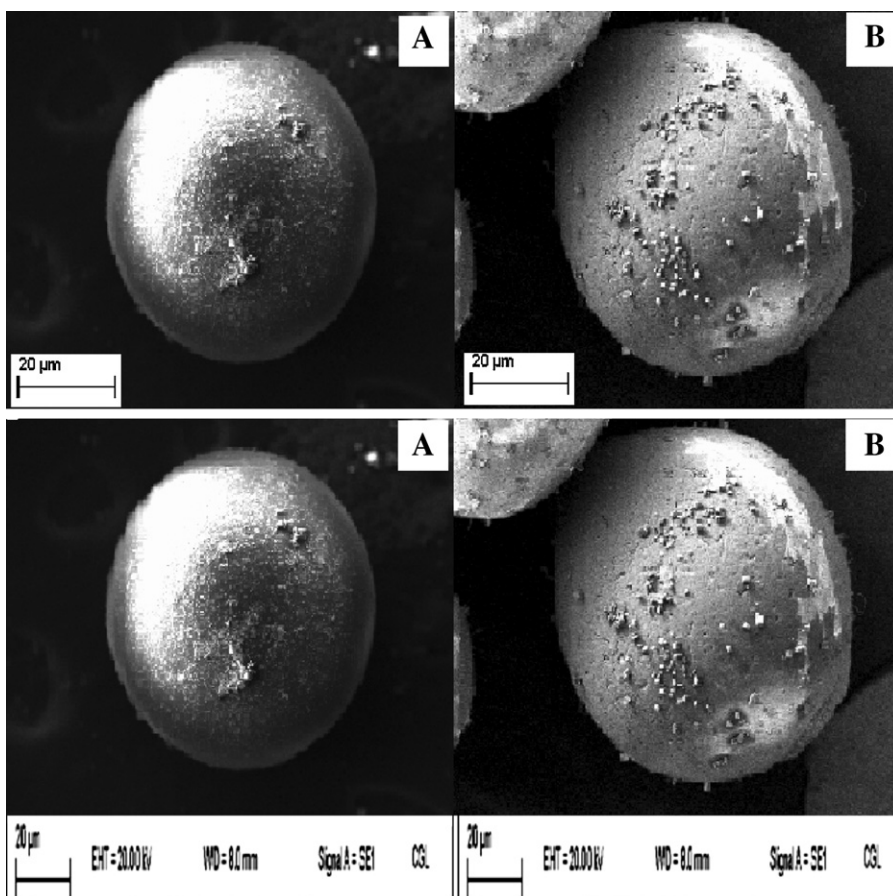


Fig. 1. FE SEM images of polymer supported Schiff base (A) and polymer supported Cu(II) Schiff base complex (B).

which suggests the formation of metal complex with the polymer anchored ligand.

### 3.1.2. IR spectral study

A partial list of the IR spectral data of Schiff base and supported complex along with their respective neat complex are presented in Table 1. In 4-acetylpyridine thiosemicarbazone (L) the infrared bands for the  $\text{-NH}_2$  and  $\text{NH}$  groups appeared at  $3456$  and  $3170\text{ cm}^{-1}$ , respectively. The bands due to  $\nu(\text{C}=\text{S})$  and  $\nu(\text{C}=\text{N})$  groups appeared at  $1110$  and  $1635\text{ cm}^{-1}$ . On complexation the bands respect to  $\nu(\text{C}=\text{S})$  and  $\nu(\text{C}=\text{N})$  are shifted lower frequency. This suggests that the ligand acts as bidentate chelating agent coordinated through 'N' (azomethine) and 'S' atom [27,28]. The pyridine ring vibrations are quite similar to those of the phenyl ring which was assigned at  $1598$ ,  $1572$ ,  $1479$  and  $766\text{ cm}^{-1}$  [29,30]; these bands are existed in 4-acetylpyridine thiosemicarbazone copper complex; this mean that the pyridine ring not participated in the complexation. In  $[\text{Cu}(\text{L})(\text{Cl})_2]$  complex, new absorption bands at  $530\text{ cm}^{-1}$ ,  $323\text{ cm}^{-1}$  and  $354\text{ cm}^{-1}$  are assigned to  $\nu(\text{Cu}-\text{N})$  [31],  $\nu(\text{Cu}-\text{S})$  [32] and  $\nu(\text{Cu}-\text{Cl})$  [33], respectively.

In the case of immobilized complex, the FT-IR spectra of polymer supported Schiff base ligand and polymer supported complex was studied. The intensity of the IR spectrum of polymer supported metal complex was weak due to the low concentration of the complex. The IR spectrum of supported complex is similar to that of the free metal complex. In polymer supported Schiff base ligand, the sharp  $\text{C}-\text{Cl}$  peak (due to  $\text{-CH}_2\text{Cl}$  groups) at  $1264\text{ cm}^{-1}$  in the starting polymer was seen as a weak band or absent [34]. The band for the  $\text{-NH}_2$  group in free Schiff base ligand was shifted to lower frequency after attachment of chloromethylated polymer to the

4-acetylpyridine thiosemicarbazone.

### 3.1.3. TGA-DTA studies

Thermal stability of complex was investigated using TGA-DTA at a heating rate of  $10^\circ\text{C}/\text{min}$  in air over a temperature range of  $30\text{--}600^\circ\text{C}$ . TGA curves of polymer supported Schiff base ligand and Cu(II) complex are shown in Fig. 3. Polymer supported Schiff base ligand decomposed in the temperature range  $370\text{--}380^\circ\text{C}$ . After complexation of copper metal on polymer supported ligand, thermal stability of the immobilized complex improved by  $20\text{--}30^\circ\text{C}$ . Polymer supported Cu(II) Schiff base complex decomposed at  $390\text{--}400^\circ\text{C}$ . So from the thermal stability, it concludes that polymer supported metal complex degraded at considerably high temperature.

### 3.1.4. Electronic spectral studies and magnetic moment

The electronic spectra of both 4-acetylpyridine thiosemicarbazone ligand (L) and its copper complex were measured in DMSO and shown in Fig. 4. Within the UV spectrum of the ligand, two absorption bands are observed at the range  $202\text{--}260\text{ nm}$  which assigned to  $\pi \rightarrow \pi^*$  transition [35] and the second appeared at the range  $285\text{--}360\text{ nm}$  due to intraligand  $n \rightarrow \pi^*$  transition [36,37]. These absorptions also present in the spectra of the copper complex but they are shifted. This shift in the spectra of the complex attributed the complexation behavior of the ligand and supports the coordination of the ligand to metallic ion. The electronic spectrum of the  $[\text{Cu}(\text{L})(\text{Cl})_2]$  complex exhibits band at  $420\text{ nm}$  (sh.) that is assigned to  $d \leftrightarrow d$  transition [38]. The magnetic moment for copper complex is found to be  $1.73\text{ BM}$ . This value suggests square planar geometry around copper(II) ion.

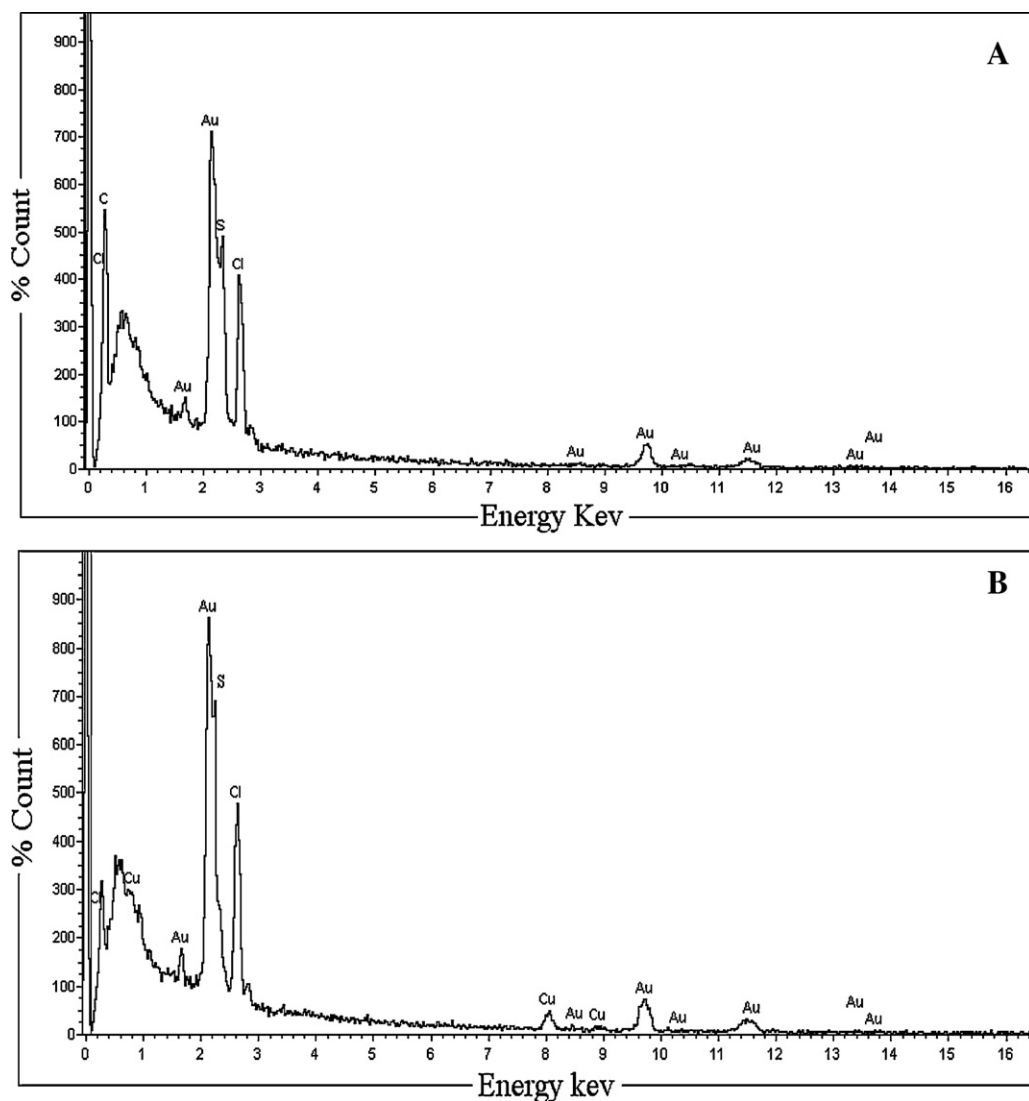


Fig. 2. EDX images of polymer supported Schiff base (A) and polymer supported Cu(II) Schiff base complex (B).

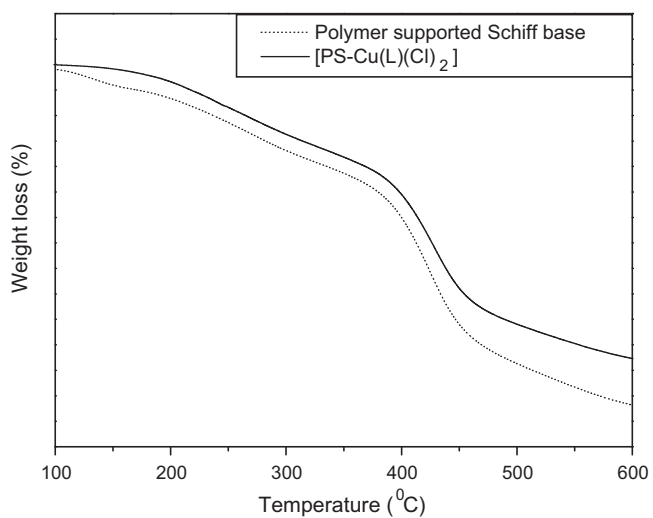


Fig. 3. Thermogravimetric weight loss plots for polymer supported Schiff base and polymer supported Cu(II) Schiff base complex.

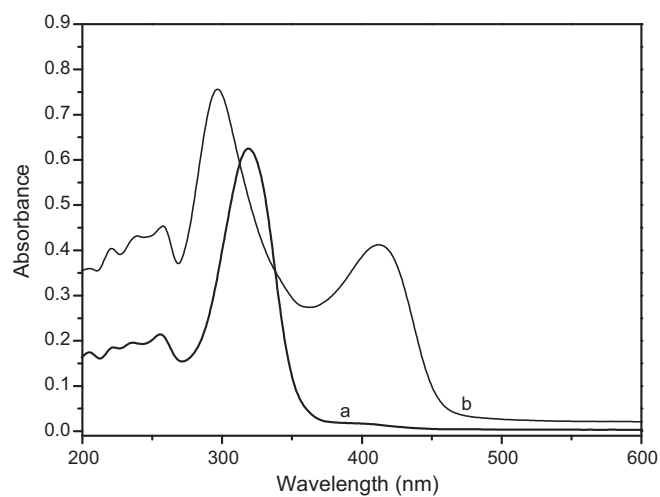


Fig. 4. Electronic spectra of 4-acetylpyridine thiosemicarbazone Schiff base (a) and [Cu(L)(Cl)<sub>2</sub>] complex (b).

### 3.1.5. DRS-UV spectroscopy

The electronic spectrum of the polymer supported metal Schiff base complex was recorded in diffuse reflectance spectrum mode as MgCO<sub>3</sub>/BaSO<sub>4</sub> disc due to their solubility limitations in common organic solvents. The diffuse reflectance spectra of Cu(II) complex was almost identical before and after supporting on polymer, indicating the complex maintains its geometry after supported. The UV-vis spectrum (DRS) is shown in Fig. 5. For example, in the spectrum of polymer supported copper complex, a absorption band at ranges 320–380 nm is observed when highly concentrated sample was used to record the spectrum and this is due to intraligand  $n \rightarrow \pi^*$  transition. A band around 415–425 nm (weak) is due to  $d-d$  transition in the complex and indicates a square-planar structure present on the polymer support. Based on the above results of elemental analysis, IR, electronic spectra, magnetic moment measurements and thermal analysis, the structure of the copper(II) complex is suggested and is given in Scheme 1.

### 3.2. Catalytic activity

Since polymer supported metal systems exhibit catalytic activity in a wide range of the industrially important processes and have been extensively studied, we decided to investigate the catalytic activity of polymer supported Cu(II) Schiff base complex in the oxidation of alkenes, alkanes and aromatic alcohols at room temperature with H<sub>2</sub>O<sub>2</sub> as oxygen source.

#### 3.2.1. The effect of oxidants on the oxidation of styrene catalyzed by PS-[Cu(L)(Cl)<sub>2</sub>]

In the catalytic oxidation of alkenes the choice of oxygen donor and solvent is importance. In this study, we investigated the ability of different oxidants, such as NaOCl, NaIO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, KHSO<sub>5</sub> and tert-butylhydroperoxide, in the oxidation of styrene catalyzed by the heterogeneous Cu(II) complex. The results are summarized in Table 2. When NaOCl, NaIO<sub>4</sub> and tert-butylhydroperoxide were used as the oxygen source in acetonitrile, only low conversion of styrene was detected in the reaction mixture. The use of KHSO<sub>5</sub> was not favored because of disadvantages such as using a buffered media during the oxidation reactions. The results show that in the presence of the catalyst, H<sub>2</sub>O<sub>2</sub> is the best oxygen source, because of good oxidation conversions and high solubility in the CH<sub>3</sub>CN.

**Table 2**

Oxidation of styrene using different oxidants and solvents catalyzed by polymer supported Cu(II) Schiff base complex.

Entry	Solvent	Oxidant	Conversion (%) <sup>a</sup>
1	CH <sub>3</sub> CN	NaOCl	45
2	CH <sub>3</sub> CN	NaIO <sub>4</sub>	81
3	CH <sub>3</sub> CN	H <sub>2</sub> O <sub>2</sub>	98
4	CH <sub>3</sub> CN	Tert-butylhydroperoxide	25
5	CH <sub>3</sub> CN	KHSO <sub>5</sub>	68
6	CH <sub>3</sub> OH	H <sub>2</sub> O <sub>2</sub>	71
7	CH <sub>3</sub> CH <sub>2</sub> OH	H <sub>2</sub> O <sub>2</sub>	62
8	CH <sub>3</sub> COCH <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	78

Reaction condition: styrene (5 mmol), oxidant (10 mmol), solvent (10 ml), room temperature and time (6 h).

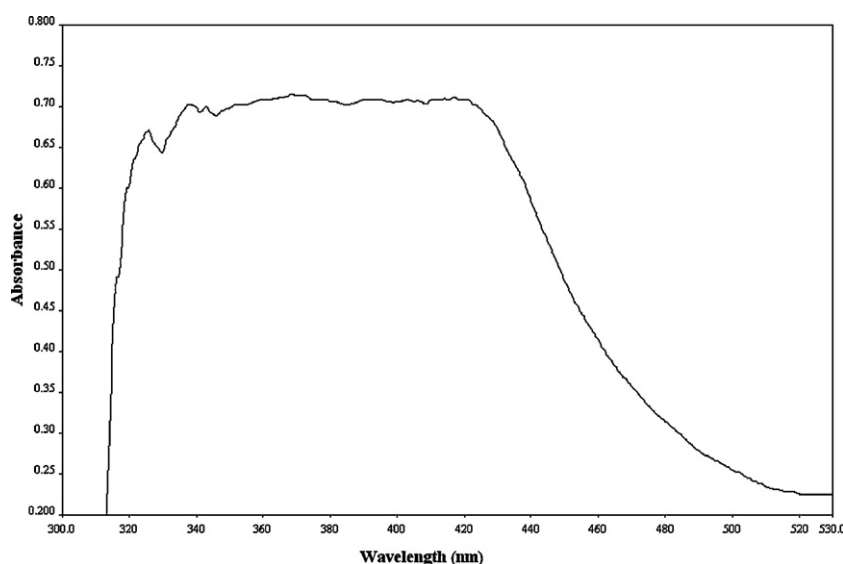
<sup>a</sup> Determined by GC.

#### 3.2.2. The effect of solvent on the oxidation of styrene catalyzed by PS-[Cu(L)(Cl)<sub>2</sub>]

The oxidation of styrene was studied in various solvents at room temperature (Table 2). Methanol, ethanol, acetone and acetonitrile were used as solvent. Among them, acetonitrile was chosen as the reaction medium, because highest conversion was obtained in acetonitrile solvent. The higher catalytic activity in acetonitrile is attributed to the polarity of the solvent and solubility of H<sub>2</sub>O<sub>2</sub> in the solvent.

#### 3.2.3. Oxidation of alkenes with H<sub>2</sub>O<sub>2</sub> catalyzed by PS-[Cu(L)(Cl)<sub>2</sub>]

The above optimized reaction conditions could be applied to the oxidation reaction of other olefins by polymer supported Cu(II) catalyst and the results are shown in Table 3. Reactions were performed at room temperature under air in CH<sub>3</sub>CN containing alkene, oxidant and catalyst. This catalyst efficiently converts olefins to their corresponding allylic products. Styrene was converted to benzaldehyde in high yield. In the oxidation of cyclohexene, allylic products 2-cyclohexene-1-one and 2-cyclohexene-1-ol were produced. Substituted styrene produced selectively corresponding aldehydes. Acetophenone was detected in the oxidation of  $\alpha$ -methyl styrene as major product. trans-Stilbene was also oxidized by this heterogeneous catalyst in high yields. trans-Stilbene gives benzaldehyde as major product with benzil. This catalytic system shows a good activity in the case of limonene and  $\alpha$ -pinene. In the oxidation of  $\alpha$ -pinene, the major products were verbenone and



**Fig. 5.** DRS-UV-vis absorption spectra of polymer supported Cu(II) Schiff base complex.

**Table 3**  
Oxidation of alkenes with 30% H<sub>2</sub>O<sub>2</sub> catalyzed by [Cu(L)(Cl)<sub>2</sub>] and PS-[Cu(L)(Cl)<sub>2</sub>] complex.

Entry	Olefins	Conversion (%) <sup>a</sup> /time (h)		Product selectivity (%) <sup>a</sup> ([PS-Cu(L)(Cl) <sub>2</sub> ]/[Cu(L)(Cl) <sub>2</sub> ])
		[PS-Cu(L)(Cl) <sub>2</sub> ]	[Cu(L)(Cl) <sub>2</sub> ]	
1	Styrene	98/6	88/6	Benzaldehyde (92/83) Styrene oxide (8/17)
2	Cyclohexene	82/6	74/6	2-Cyclohexene-1-one (72/65) 2-Cyclohexene-1-ol (21/21) Cyclohexene epoxide (7/14)
3	α-Methyl styrene	88/6	79/6	Acetophenone (100/91)
4	α-Pinene	55/6	48/6	Verbenol (32/28), verbenone (55/47), α-pinene oxide (13/25)
5	Limonene	56/6	47/6	Carvenol (25/21), Carvenone (67/61), limonene oxide (1,2) (8/18)
6	trans-Stilbene	76/6	68/6	Benzaldehyde (78/69) Benzil (16/20), trans-stilbene oxide (6/11)
7	4-Chlorostyrene	83/6	77/6	4-Chloro benzaldehyde (88/78), 4-Chlorostyrene epoxide (12/22)
8	4-Methylstyrene	79/6	68/6	4-Methyl benzaldehyde (86/72), 4-methylstyrene epoxide (14/28)
9	4-Nitrostyrene	71/6	67/6	4-Nitro benzaldehyde (84/66) 4-Nitro styrene oxide (16/34)
10	1-Hexene	47/6	39/6	2-Hexanone (98/84)

Reaction condition: alkene (5 mmol), 30% H<sub>2</sub>O<sub>2</sub> (10 mmol), CH<sub>3</sub>CN (10 ml), room temperature.

<sup>a</sup> Determined by GC.

verbenol. Limonene selectively oxidized to Carvone and Carveol with other coproducts. Blank experiment in the presence of oxidant under the same experimental conditions in the absence of catalyst was also investigated in the oxidation of styrene. The obtained results showed that H<sub>2</sub>O<sub>2</sub> has poor ability to oxidize the styrene.

#### 3.2.4. Oxidation of alkanes with H<sub>2</sub>O<sub>2</sub> catalyzed by PS-[Cu(L)(Cl)<sub>2</sub>]

The catalytic oxidation of alkanes with 30% H<sub>2</sub>O<sub>2</sub> under mild reaction conditions is especially an interesting topic, because direct functionalization of inactivated C–H bonds in saturated hydrocarbons usually requires drastic reaction conditions such as high pressure and high temperature. As shown in Table 4, we have found that the supported copper catalyst is an efficient catalyst for the oxidation of saturated hydrocarbons with H<sub>2</sub>O<sub>2</sub> at room temperature. Ethylbenzene and propylbenzene only produced the corresponding ketones. Toluene selectively converted to benzaldehyde. In the case of adamantane, the 1-adamantanol and 2-adamantanone were produced in the reaction mixture.

#### 3.2.5. Oxidation of aromatic alcohols with H<sub>2</sub>O<sub>2</sub> catalyzed by PS-[Cu(L)(Cl)<sub>2</sub>]

The selective oxidation of alcohols into their corresponding carbonyl compounds is one of the fundamental reactions in organic chemistry. Selective oxidation of aromatic alcohols to aldehydes was investigated with H<sub>2</sub>O<sub>2</sub> under mild reaction conditions by polymer supported copper catalyst. Experimental results are shown in Table 5. Benzyl alcohol selectively converted to benzaldehyde. Substituted benzyl alcohols are also oxidized to corresponding aldehydes. In all above cases trace amount of acids were observed. On the other hand, 1-phenyl ethanol selectively converted to acetophenone on oxidation with this catalyst.

### 3.3. Antimicrobial studies

The Schiff base ligand and copper(II) complex were screened in vitro for their microbial activity against two bacterial species using the well diffusion method. These compounds were found to exhibit considerable activity against Gram +ve (*S. aureus*) and Gram –ve (*E. coli*). The test solutions were prepared in N,N-dimethylformamide and the results are summarized in Table 6. Blank experiment with CuCl<sub>2</sub> was carried out under identical experimental conditions and showed the inability of the complex to inhibit the bacterial growth. The effectiveness of an antimicrobial agent in sensitivity is based on the zones of inhibition. The

diameter of the zone is measured to the nearest millimeter (mm). The standard error for each assay is presented in the parenthesis. From the results (Table 6), it has been observed that copper complex showed slight better activity than the free ligand. This can be explained by Tweedy's chelation theory [39]. This copper complex possesses activity and its effectiveness is greater than the standard drug Streptomycin. The inhibition activity of the compounds increases with increase in the concentration of the solution.

## 4. Influence of support

In order to demonstrate the effect of supporting on the catalytic activity of homogeneous copper complex in the oxidation of alkene, alkane and aromatic alcohol with hydrogen peroxide, we repeated all reactions with the same reaction conditions and [Cu(L)(Cl)<sub>2</sub>] catalyst, substrate, H<sub>2</sub>O<sub>2</sub> in CH<sub>3</sub>CN. The obtained results are summarized in Tables 3–5. The obtained results showed that the production of by-products in the heterogenized system decreased in comparison with the homogeneous system in the alkene, alkane and alcohol oxidation. Selectivity and stability of the heterogeneous catalyst are better than the homogeneous catalyst. On the other hand, the heterogeneous catalyst can be recovered several times without loss of its activity. The most disadvantageous of homogeneous complex is the catalysts degradation in the presence of oxidant, while, the heterogenized complex can be reused several times without significant loss of its activity.

Many efficient heterogeneous catalysts have been reported for the oxidation of alkenes, alkanes and aromatic alcohols with 30% H<sub>2</sub>O<sub>2</sub> [23,40–42]. Comparison of this catalyst with previously reported systems reveals that the present system gives better conversion than other catalyst.

## 5. Stability and recycling of catalyst

To check the leaching of metal into the solution during the reaction, styrene oxidation was carried out under the optimum reaction conditions. The reaction was stopped after the reaction proceeds 3 h. The separated filtrate was allowed to react for another 3 h under the same reaction condition, but no further increment in conversion was observed in gas chromatographic analyses. The UV–vis spectroscopy was also used to determine the stability of this heterogeneous catalyst. The UV–vis spectra of the reaction solution, at the first run, did not show any absorption peaks characteristic of copper metal, indicating that the leaching of metal did not take place during the course of the oxidation reaction. These results sug-

**Table 4**  
Oxidation of alkanes with 30% H<sub>2</sub>O<sub>2</sub> catalyzed by [Cu(L)(Cl)<sub>2</sub>] and PS-[Cu(L)(Cl)<sub>2</sub>] complex.

Entry	Alkane	Conversion (%) <sup>a</sup> /time (h)		Product selectivity (%) <sup>a</sup> ([PS-Cu(L)(Cl) <sub>2</sub> ]/[Cu(L)(Cl) <sub>2</sub> ])
		[PS-Cu(L)(Cl) <sub>2</sub> ]	[Cu(L)(Cl) <sub>2</sub> ]	
1	Ethyl benzene	76/8	70/8	Acetophenone (100/92)
2	Propylbenzene	61/8	56/8	Ethylphenyl ketone (100/89)
3	Toluene	41/8	35/8	Benzaldehyde (96/81)
4	Adamantane	52/8	44/8	1-Adamantanol (76/61) 2-Adamantanone (24/39)

Reaction condition: alkane (5 mmol), 30% H<sub>2</sub>O<sub>2</sub> (10 mmol), CH<sub>3</sub>CN (10 ml), room temperature.

<sup>a</sup> Determined by GC.

**Table 5**  
Oxidation of aromatic alcohols with 30% H<sub>2</sub>O<sub>2</sub> catalyzed by [Cu(L)(Cl)<sub>2</sub>] and PS-[Cu(L)(Cl)<sub>2</sub>] complex.

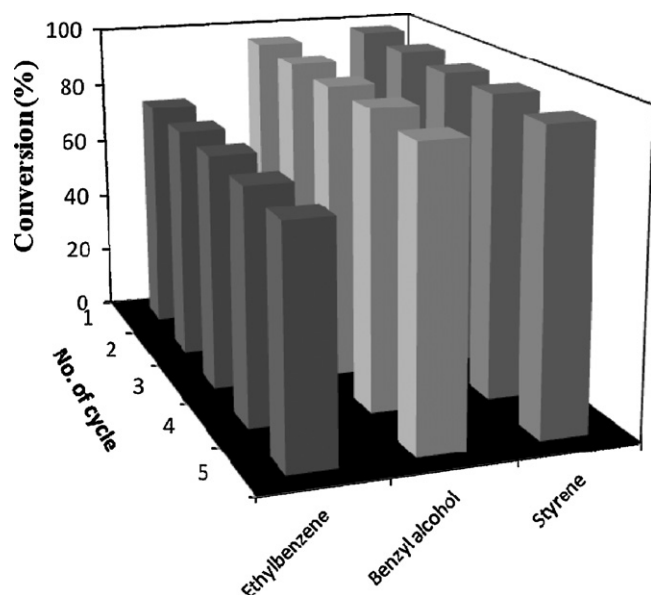
Entry	Aromatic alcohol	Conversion (%) <sup>a</sup> /time (h)		Product Selectivity (%) <sup>b</sup> ([PS-Cu(L)(Cl) <sub>2</sub> ]/[Cu(L)(Cl) <sub>2</sub> ])
		[PS-Cu(L)(Cl) <sub>2</sub> ]	[Cu(L)(Cl) <sub>2</sub> ]	
1	Benzyl alcohol	96/6	89/6	Benzaldehyde (97/86) Benzoic acid (3/14)
2	4-methylbenzyl alcohol	81/6	77/6	4-Methyl benzaldehyde (90/74) 4-Methyl benzoic acid (10/26)
3	4-nitrobenzyl alcohol	84/6	76/6	4-Nitro benzaldehyde (88/69) 4-Nitro benzoic acid (12/31)
4	1-phenyl ethanol	77/6	69/6	Acetophenone (100/89)

Reaction condition: aromatic alcohol (5 mmol), 30% H<sub>2</sub>O<sub>2</sub> (10 mmol), CH<sub>3</sub>CN (10 ml), room temperature.

<sup>a</sup> Determined by GC.

**Table 6**  
Antibacterial activities of copper(II) Schiff base complex.

Compound	Diameter of inhibition zone (mm)							
	<i>E. coli</i> (Gram -ve)				<i>S. aureus</i> (Gram +ve)			
	50 ppm	75 ppm	100 ppm	150 ppm	50 ppm	75 ppm	100 ppm	150 ppm
L	22.0 (±0.35)	22.0 (±0.58)	24.0 (±0.65)	24.0 (±0.24)	20.0 (±1.65)	22.0 (±0.58)	22.0 (±0.38)	26.0 (±0.80)
[Cu(L)(Cl) <sub>2</sub> ]	24.0 (±0.58)	24.0 (±0.80)	26.0 (±0.77)	26.0 (±0.54)	22.0 (±0.40)	24.0 (±0.54)	24.0 (±0.51)	26.0 (±0.65)
Streptomycin	11.3 (±1.4)	12.0 (±0.8)	13.0 (±0.12)	13.5 (±0.8)	11.9 (±0.5)	12.0 (±0.12)	12.5 (±0.12)	13.0 (±0.50)



**Fig. 6.** Recycling efficiency for the oxidation of styrene, ethyl benzene and benzyl alcohol with [PS-Cu(L)(Cl)<sub>2</sub>] complex. Reaction condition: [substrate] = 5 mmol, [30% H<sub>2</sub>O<sub>2</sub>] = 10 mmol, catalyst (0.05 g), CH<sub>3</sub>CN (10 ml), room temperature, time (6 h).

gest that this catalyst was heterogeneous in nature. IR spectrum of the recycled catalyst was quite similar to that of 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 transition metal ions. The results indicate that this complex is stable to be recycled for the oxidation reaction without much loss in activity.

The recyclability of the catalyst is important for the catalysis reaction. The recycling experiment also confirms the heterogenization of complex into polymer. To investigate the reusability of polymer supported copper Schiff base complex, this catalyst was separated by filtration after the first catalytic reaction finished. For the next reaction cycle, we recover the catalyst by washing with solvent and dried under vacuum then subjected to the second run under the same reaction conditions. The catalytic run was repeated with further addition of substrates in appropriate amount under optimum reaction conditions and the nature and yield of the final products were comparable to that of the original one. Fig. 6 illustrates the reusability of the catalyst for the oxidation of styrene, ethylbenzene and benzyl alcohol during five recycles. It was found that the catalytic activity did not change significantly after five repeat runs.

## 6. Conclusions

In summary, we have successfully synthesized polymer anchored Cu(II) Schiff base complex. The developed heterogeneous catalyst shows high catalytic activity in oxidation of alkene, alkane and aromatic alcohol. The results show that the immobilized catalyst is slightly more active than its homogeneous analogue. The heterogeneous and homogeneous complexes produce selectively allylic oxidation products for alkenes, alcohols and ketones from alkanes and aldehydes from aromatic alcohols. Another important



factor is the stability and recyclability of the catalyst under the reaction conditions used. This heterogeneous catalyst shows no significant loss of activity in the recycling experiments. The active sites do not leach out from the support and thus can be reused without appreciable loss of activity, indicating that the anchoring procedure was effective as observed from UV–vis spectroscopy. Leaching test indicates that the catalytic reaction is mainly heterogeneous in nature. The reusability of this catalyst is high and can be reused five times without significant decrease in its initial activity. We hope that the present catalytic systems would be useful to synthesize industrially important organic compounds.

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### References

- [1] G. Strukul (Ed.), *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, Kluwer Academic Publishers, Dordrecht, Netherlands, 1992.
- [2] J. Muzart, *J. Mol. Catal. A: Chem.* 276 (2007) 62.
- [3] N. Mizuno, K. Yamaguchi, K. Kamata, *Coord. Chem. Rev.* 249 (2005) 1944.
- [4] M. Salavati Niasari, S. Nezamoddin Mirsattari, *J. Mol. Catal. A: Chem.* 268 (2007) 50.
- [5] K.C. Gupta, A.K.R. Suta, *React. Funct. Polym.* 68 (2008) 12.
- [6] S. Mukherjee, S. Samanta, B.C. Roy, A. Bhaumik, *Appl. Catal. A: Gen.* 301 (2006) 79.
- [7] M.R. Maurya, A.K. Chandrakar, S. Chand, *J. Mol. Catal. A: Chem.* 270 (2007) 225.
- [8] M. Mureseanu, V. Părvulescu, R. Ene, N. Cioatera, T.D. Pasatoiu, M. Andruh, *J. Mater. Sci.* 44 (2009) 6795.
- [9] In: B. Fredrich, W. Gerhartz (Eds.), *Ullmann's Encyclopedia of Industrial Chemistry*, vol. A3, Wiley-VCH, Weinheim, New York, 1985, p. 470.
- [10] R.A. Sheldon, J.K. Kochi, *Metal Catalyzed Oxidation of Organic Compounds*, Academic Press, New York, 1981.
- [11] A.E. Shilov, G.B. Shul'pin, *Chem. Rev.* 97 (1997) 2879.
- [12] J.I. Kroschwitz, K. Othmer, *Encyclopedia of Chemical Technology*, Wiley-Interscience, New York, 1992.
- [13] F. Ullmann, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Verlag, Weinheim, Germany, 2003.
- [14] K.R. Gruenwald, A.M. Kirillov, M. Haukka, J. Sanchiz, A.J.L. Pombeiro, *Dalton Trans.* (2009) 2109.
- [15] A. Sakthivel, S.E. Dapurkar, P. Selvan, *Appl. Catal. A: Gen.* 246 (2003) 283.
- [16] S.E. Dapurkar, A. Sakthivel, P. Selvan, *New J. Chem.* 27 (2003) 1184.
- [17] J. Handzlik, J. Ogonowski, J. Stoch, M. Mikołajczyk, *Catal. Lett.* 101 (2005) 65.
- [18] M. Mureseanu, V. Părvulescu, A.R. Ene, A.N. Cioatera, T.D. Pasatoiu, M. Andruh, *J. Mater. Sci.* 44 (2009) 6795.
- [19] Z. Lei, *React. Funct. Polym.* 43 (2000) 139.
- [20] M. Salvati-Niasari, *Inorg. Chem. Commun.* 8 (2005) 174.
- [21] W. Thitsartarna, E. Gularib, S. Wongkasemjita, *Appl. Organomet. Chem.* 22 (2008) 97.
- [22] V.B. Valodkar, G.L. Tembe, M. Ravindranathan, H.S. Rama, *J. Mol. Catal. A: Chem.* 223 (2004) 31.
- [23] M.R. Maurya, A. Arya, P. Adao, J.C. Pessoa, *Appl. Catal. A: Gen.* 351 (2008) 239.
- [24] V. Mirkhani, M. Moghadam, S. Tangestaninejad, B. Bahramian, *Appl. Catal. A: Gen.* 311 (2006) 43.
- [25] A.I. Vogel, *Test Book of Practical Organic Chemistry*, 5th ed., Longman, London, 1989.
- [26] M.S. Refat, H.K. Ibrahim, S.Z.A. Sowellim, M.H. Soliman, E.M. Saeed, *J. Inorg. Organomet. Polym.* 19 (2009) 521.
- [27] S. Chandra, A. Kumar, *Spectrochim. Acta A* 68 (2007) 1410.
- [28] S. Chandra, K. Gupta, *Trans. Met. Chem.* 27 (2002) 196.
- [29] J.H.S. Green, W. Kynaston, H.M. Paisley, *Spectrochim. Acta* 19 (1963) 549.
- [30] A.R. Katritzky, A.P. Ambler (Eds.), *Physical Methods in Heterocyclic Chemistry*, vol. II, Academic Press, New York, 1963, p. 276.
- [31] S.S. Kandil, G.B. El-Hefnawy, *Trans. Met. Chem.* 28 (2003) 168.
- [32] K.H. Reddy, M.R. Reddy, K.M. Raju, *Ind. J. Chem.* 38A (1999) 299.
- [33] J.R. Ferraro, *Low Frequency Vibration of Inorganic and Coordination Compounds*, Plenum Press, New York, 1971.
- [34] M.D. Angelino, P.E. Laibinis, *Macromolecules* 31 (1998) 7581.
- [35] W. Barnum, *J. Inorg. Nucl. Chem.* 21 (1961) 221.
- [36] R.H. Holm, F.A. Cotton, *J. Am. Chem. Soc.* 80 (1958) 5658.
- [37] F.A. Cotton, C.W. Wilkinson, *Advanced Inorganic Chemistry*, 3rd ed., Interscience Publisher, New York, 1972.
- [38] H.B. Gray, C.J. Ballhausen, *J. Am. Chem. Soc.* 85 (1963) 260.
- [39] B.G. Tweedy, *Phytopathology* 55 (1964) 910.
- [40] V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork, N. Rasouli, *Catal. Commun.* 9 (2008) 2411.
- [41] A. Jia, L.L. Lou, C. Zhang, Y. Zhang, S. Liu, *J. Mol. Catal. A: Chem.* 306 (2009) 123.
- [42] J. Hu, K. Li, W. Li, F. Ma, Y. Guo, *Appl. Catal. A: Gen.* 364 (2009) 211.