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Synthesis, characterization and catalytic activity of polymer anchored transition metal complexes toward oxidation reactions

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Abstract The polymer-anchored Schiff base complexes of Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) were prepared by reacting polystyrene amine with 2-pyridinecarbaldehyde followed by loading of metal atom in methanol. These complexes were characterized by using different physico-chemical and spectroscopic methods. The catalytic activity of these polymer-supported metal catalysts was tested for the oxidation of various olefins and alcohols. Influence of various reaction parameters, such as reaction temperature, reaction time, oxidant, substrate-to-oxidant mole ratio and nature of solvent, was studied for the oxidation of cyclohexene with these catalysts. Among the catalysts studied, Cu-Cat showed higher catalytic activity toward oxidation reactions than the other catalysts. Moreover, hot filtration experiments proved that these catalysts are truly heterogeneous and can be reused a number of times without significant loss of activity.

Introduction

The oxidation of hydrocarbons to oxygenic compounds is a pivotal reaction in organic chemistry, both for fundamental research and industrial manufacturing [1, 2]. Oxidation of olefins and 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 [3]. Now, from both economic and environmental points of view, much attention has recently been focused on the aerobic catalytic oxidation of hydrocarbons to oxygenic compounds using metal catalysts. Transition metal complexes are widely used in homogeneous and heterogeneous catalytic oxidations of different alkenes, alkynes, alcohols, halides, phenols etc [4, 5]. 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 [6, 7]. In 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 recovery of the catalyst from reaction mixture and recycling. Transition metals supported on materials such as alumina [8], amorphous silicates [9], polymers [10] and zeolites [11] are commonly employed in heterogeneous catalysis.

Polystyrene is one of the most widely 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 [12, 13] and have shown lower leaching of palladium during cross-coupling. This encouraged us to investigate the functionalized polystyrene resin-supported transition metal complexes for the oxidation reactions. We have already

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reported the use of a polystyrene-anchored transition metal complex as an air-stable, active, and reusable catalyst in various organic reactions [14–16].

Herein, we report the synthesis of new functionalized transition metal complexes anchored to polystyrene via nitration and then reduction to amino functionality followed by Schiff base condensation. The Schiff base anchored in the polymer matrix has been designed in such a way that it could interact covalently with the metal centers and thus generate a suitable heterogeneous catalyst. These polymer-anchored complexes showed high catalytic activity in the oxidation reactions of olefins and alcohols. Further, this polymer-anchored complex offers easy catalyst recovery and excellent recycling efficiency.

Experimental

All the reagents were of analytical grade and used as such without further purification. Solvents were purified and dried according to standard procedures [17]. The liquid substrates were predistilled and dried by appropriate molecular sieve, and the solid substrates were recrystallized before use. Macroporous polystyrene beads cross-linked with divinylbenzene were purchased from Aldrich Chemical Company, USA. Other reagents were purchased from Merck.

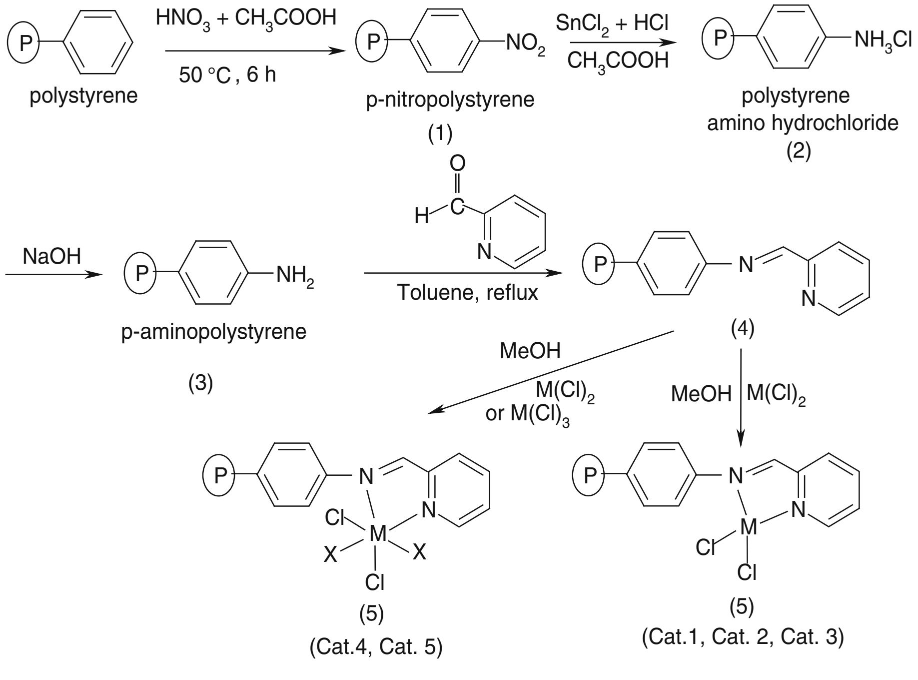
A Perkin-Elmer, USA, 2400C elemental analyzer was used to collect microanalytical data (C, H and N). The metal content in the polymer-anchored complex was analyzed using a Varian, USA, AA240 atomic absorption spectrophotometer (AAS). The reaction products were analyzed by Varian, USA, 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a flame ionization detector. All reaction products were identified by using an Agilent, USA, GC-MS (QP-5050). Surface morphology of functionalized polystyrene ligand and metal complex was analyzed using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility. The thermal stability of the immobilized catalyst was determined using a Mettler Toledo, Switzerland, TGA/DTA 851. Magnetic moment of the complexes was determined at room temperature using Guoy's method. The FTIR spectra of the immobilized catalyst were recorded on a Perkin-Elmer, USA, FTIR 783 spectrophotometer using KBr pellets. Diffuse reflectance UV–Vis spectra were taken using a Shimadzu, Japan, UV-2401PC double beam spectrophotometer having an integrating sphere attachment for solid samples.

Catalytic oxidation reaction

The catalytic oxidation reaction was carried out in a 50-mL flask keeping in a thermostatted oil bath. In a typical reaction, substrate (5 mmol) and oxidant (10 mmol) were taken in 10 mL solvent in the flask, and then the catalyst (0.88 mmol) was added. When the reaction was carried out under oxygen atmosphere, oxygen gas was purged into the flask continuously. After the reaction was completed, the catalyst was separated by filtration. The product was analyzed by gas chromatography (Varian 3400) using a FID. The formation of product was confirmed by GC-MS (Agilant QP-5050).

Preparation of catalyst

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



Scheme 1 Synthesis of the polymer-anchored metal complexes. P = Polystyrene frame work, M = Cu (Cat.1), Co (Cat.2), Ni (Cat.3), Mn (Cat.4), Fe (Cat.5); X = H_2O or Cl

Preparation of the polymer-anchored catalyst (5)

The polymer-anchored 2-pyridinecarbaldehyde ligand (4) was synthesized by the procedure similar to that described in our previous report [18].

Polymer-anchored 2-pyridinecarbaldehyde ligand (1 g) was taken in methanol (10 mL). In the reaction mixture, 1% (w/v) methanolic solution of metal chloride was added dropwise over a period of ca. 30 min under constant stirring. The mixture was refluxed for 24 h, and the complex was filtered off, washed thoroughly with methanol until the washings were colorless and dried in room temperature under vacuum.

Results and discussion

Characterization of the polymer-anchored Schiff base complexes

Due to insolubilities of the polymer-anchored metal complexes in all common organic solvents, their characterization was limited to their physicochemical properties, chemical analysis, SEM, TGA, IR and UV–Vis spectral data. Elemental analyses of the ligand and metal complexes (Table 1) support the formulation of the complex as proposed. Metal content of catalysts determined by AAS suggests 1.4 wt% Cu, 1.8 wt% of Co, 2.3 wt% of Ni, 1.7 wt% of Mn and 2.7 wt% of Fe in the metal complexes, respectively. In Fig. 1, the SEM images of polymer-anchored Schiff base ligand (Fig. 1a) and the immobilized metal complexes on modified polystyrene (Fig. 1b, f) are shown. Pure polymer beads have a smooth and flat surface (not shown in Fig. 1). The introduction of the ligand on to 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 interaction of the metal atoms with the ligand to accommodate the fixed geometry of the complexes. Energy dispersive spectroscopy X-ray analyses (EDX analysis) of the complexes show the metal content along with C and Cl, suggesting the formation of metal complex with the anchored ligand at various sites (Fig. 2). Cl/M ratio obtained from EDX analysis is quite similar to the data obtained from elemental analysis (Table 1). The attachment of metal on the polymer matrix is confirmed from these SEM images and EDX data.

Table 1 Physical and analytical data of polymer-anchored ligand and complexes

Compound	Color	Cl %	C %	H %	N %	M %	Cl/M
PS	Colorless	–	92.5	7.6	–	–	
PS-NO$_2$	Light yellow	–	74.1	5.7	6.0	–	
PS-NH$_3$Cl	Yellow	13.3	72.0	6.7	5.8	–	
PS-NH$_2$	Pale yellow	–	84.1	7.3	6.7	–	
PS-Ligand	Brown	–	83.5	6.5	8.8	–	
Cat. 1	Brown	6.5	73.3	5.7	7.7	1.4	4.6 (4.5)
Cat. 2	Brown	7.1	72.9	5.7	7.6	1.8	3.9 (3.8)
Cat. 3	Yellowish brown	5.9	73.9	5.9	7.8	2.3	2.5 (2.3)
Cat. 4	Yellowish brown	5.2	73.2	6.1	7.7	1.7	3.1 (3.1)
Cat. 5	Dark brown	11.5	66.8	5.5	7.0	2.7	4.2 (4.0)

PS Polystyrene

Cl/M ratio obtained from EDX analysis is given in parentheses

The IR bands that can provide structural evidence for the coordination of the ligand to the central metal atom are given in Table 2. The FT–IR spectra of various catalysts prepared in this study were recorded in the ranges of 4,000–400 cm^{-1} and 500–100 cm^{-1}. The polystyrene-anchored Schiff base ligand (4) exhibits a peak at 1,640 cm^{-1} due to (C=N)$_{\text{azomethene}}$ stretching vibration. Coordination of azomethene nitrogen in the complexes is suggested by the shift of ν(C=N)$_{\text{azomethene}}$ to lower frequencies in the IR spectra of the complexes compared to the ligand [19]. Another band at 1,594 cm^{-1} in the free ligand is due to ν(C=N)$_{\text{pyridine}}$ group and is also shifted toward lower frequency on complexation [20]. This indicates that the nitrogen atom of the pyridine group is also involved in complex formation. Coordination of imine nitrogen is consistent with the presence of a band at 460, 467, 470, 465 and 470 cm^{-1} in Cat. 1, Cat. 2, Cat. 3, Cat. 4 and Cat. 5, respectively, which is due to the formation of M–N bond between the metal and azomethine nitrogen [21]. Another band at 545, 536, 540, 542 and 542 cm^{-1} in the Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) metal complexes due to the formation of metal bond with pyridine nitrogen (M–N) is also observed [22]. The far IR spectrum of these complexes exhibits a broad intense band around 315–336 cm^{-1}, which may be assigned to M–Cl [23].

The magnetic moment measurements of these complexes were carried out in the solid state at room temperature. The magnetic moment (μ) of the complexes of Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) is found to be 1.88, 2.76, 0.00, 5.84 and 5.71, respectively (Table 2). The room temperature magnetic moment of the polymeric Cu(II), Fe(III), Co(II) and Mn(II) complexes are paramagnetic in nature. On the other hand, the polymeric Ni(II) complex has been found to be diamagnetic due to spin-paired d^8 system [24]. This diamagnetic nature supports the formation of a low-spin square-planar geometry around Ni(II). The Cu(II) complex shows a magnetic moment value of 1.88 B.M. [25], a value close to the spin-only value of 1.73 B.M., expected for $S = ½$ system, while the magnetic moment value of the Co(II) complex is 2.76 B.M., which is generally arising from one unpaired

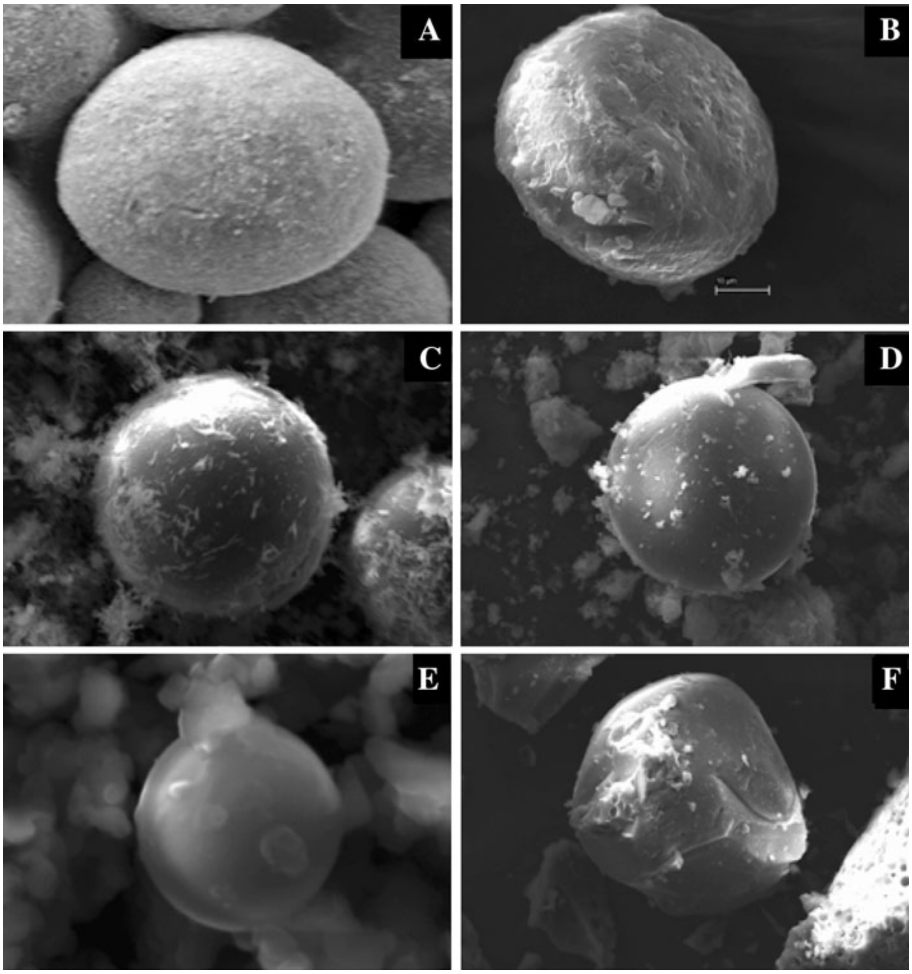


Fig. 1 FE SEM image of polymer-anchored Schiff base ligand (**a**) and polymer-anchored Cu (**b**), Co (**c**), Ni (**d**), Mn (**e**) and Fe (**f**) complexes, respectively

electron and an apparently large orbital contribution and also diagnostic of the geometry around the low-spin tetra-coordinated Co(II) atom [26]. The magnetic moment values of the Fe(III) and Mn(II) complexes support the formation of high-spin octahedral geometry [27].

The electronic spectra of all the polymeric metal catalysts have been recorded in diffuse reflectance spectrum mode as $BaSO_4$ disks due to their solubility limitations in common organic solvents. The electronic spectral bands for the Schiff base ligand and metal complexes have been given in Table 2 and Fig. 3. The polymer-anchored Schiff base ligand shows two bands at 330 nm and 375 nm that may be assigned to intraligand n–π* and π–π* transitions, respectively. These bands show blue shift on complexation. The reflectance spectrum of the Cu(II) catalyst shows two bands at 405 and 418 nm, which may be assigned to charge transfer transitions, while the shoulder at around 490 nm may be attributed to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition in a distorted tetrahedral stereochemistry [28, 29]. The electronic spectrum of the Co(II) complex showed a sharp peak at 495, which is attributed to LMCT transition [30, 31], while the absorption bands in the region 580–630 nm can be assigned to ${}^2A_{1g} \rightarrow {}^2B_{1g}$ transition [28]. The Ni(II) complex shows two peaks at ~425 nm and 532 nm that are characteristic of square planar diamagnetic Ni(II) [32]. The manganese complex exhibits a broad band around 382–452 nm, which might be due to the d–d transition of Mn(II) [33]. The electronic spectrum of the Fe(III) complex exhibits four bands at 312, 358, 440 and 627 nm. The first two peak in the UV region may be assigned to n–π* and π–π* transition [34, 35]. The medium intensity band at 440 nm may be assigned as ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (G) transitions in octahedral symmetry [28] around Fe(III). The intensities of the bands in the spectra are affected possibly due to the low loading of the metal onto the polymer backbone.

Thermal analysis of the metal complexes was carried out to find the stability of the complexes. Thermogravimetric analyses of these complexes were performed in air atmosphere at a heating rate of 10 °C min^{-1}. The TG-data of the Cat. 1–Cat. 5 are depicted in Fig. 4. From these results, the decomposition temperatures of Cat. 1–Cat. 5 are 323, 315, 308, 313 and 295, respectively. From the TG profile, it is

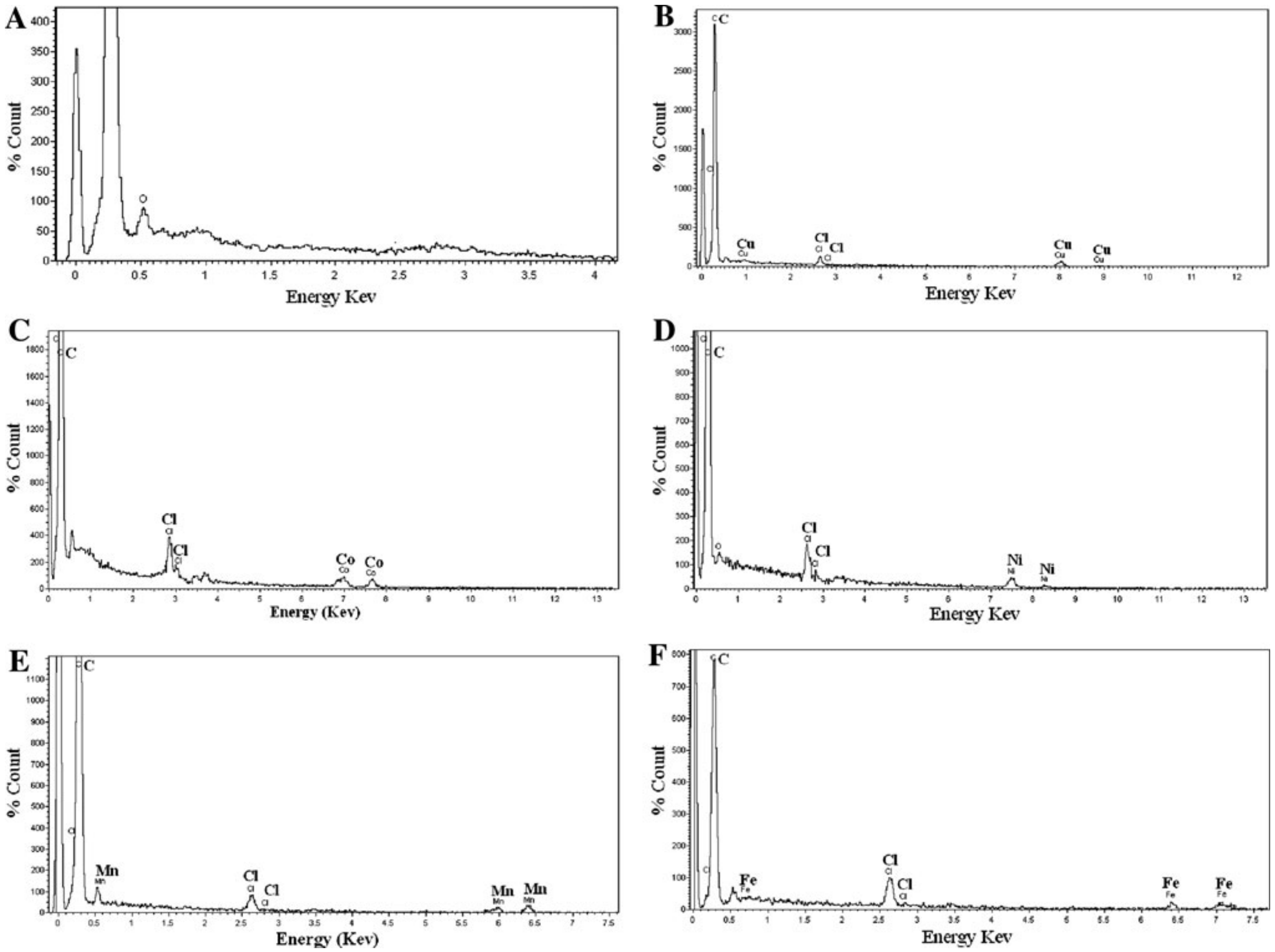


Fig. 2 EDX images of polymer-anchored Schiff base ligand (**a**) and polymer-anchored Cu (**b**), Co (**c**), Ni (**d**), Mn (**e**) and Fe (**f**) complexes, respectively

seen that the Cu(II) complex is more stable than the other complexes.

Catalytic activity

To explore the catalytic activity of the present catalysts, we performed the oxidation reaction with these catalysts. In search of suitable reaction conditions to achieve the maximum oxidation products, initial catalytic test was carried out for the oxidation of cyclohexene with polymer-anchored Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) catalysts (Scheme 2). The oxidation of cyclohexene produced 2-cyclohexene-1-one and 2-cyclohexene-1-ol as major product and also cyclohexane epoxide in minor yield. Since the performance of a successful metal-catalyzed oxidation reaction is known to be governed by a number of factors, at first, the effects of various solvents, oxidants, reaction time, reaction temperature, substrate-to-oxidant ratio and catalyst amount on the oxidation reaction were surveyed to optimize the reaction conditions for yield of product.

Effect of solvent

Solvent plays a crucial role in the yield and product distribution of oxidation reactions. In order to study the effect of solvents, several solvents were employed in the oxidation reaction of cyclohexene (5 mmol) with TBHP (10 mmol) at 60 °C keeping other parameters constant. The oxidation reaction was carried out in several polar and non-polar solvents. The selected solvent should possess certain criteria such as it should be stable and it should dissolve the substrate and oxidant. As shown in Table 3, quantitative yields were observed with polar solvents such as acetonitrile (ACN), methanol and dichloromethane (DCM). On the contrary, unsatisfactory yields were obtained with non-polar solvents like toluene and benzene. The efficiency of the catalysts for oxidation of cyclohexene in different solvents decreased in the order ACN > methanol > DCM > toluene > benzene. The higher catalytic activity in acetonitrile is attributed to high dielectric constant, polarity of solvent and better solubility of substrate

Table 2 Magnetic, IR (in cm^{-1}) and electronic spectral data of the compounds

Compound	νNO_2	νNH_3Cl	νNH_2	$\nu C{=}N$	$\nu M{-}N$	$\nu M{-}Cl$	λ_{max} (nm)	μ_{eff} (B.M.)
PS-NO_2	1520(s) 1350(s)							
PS-NH_3Cl	1520(w) 1350(w)	2545						
PS-NH_2	1520(w) 1350(w)		1625 (sh)					
PS-Ligand	1520(w) 1340(w)			1640^a 1594^b			330, 375	
Cat. 1	1520(w) 1350(w)			1614^a 1588^b	460^c 545^d	336	328, 375, 405, 418, 490	1.88
Cat. 2	1520(w) 1340(w)			1622^a 1572^b	467^c 536^d	315	309, 373, 495, 580–630	2.76
Cat. 3	1520(w) 1340(w)			1605^a 1576^b	470^c 540^d	327	312, 368, 425, 532	0.00
Cat. 4	1520(w) 1340(w)			1618^a 1570^b	465^c 542^d	325	327, 350, 382–452	5.84
Cat. 5	1520(w) 1340(w)			1626^a 1583^b	470^c 542^d	335	312, 358, 440, 627	5.71

[a] $\nu(C{=}N)_{azomethene}$;
[b] $\nu(C{=}N)_{pyridine}$;
[c] $\nu(M{-}N_{azomethene})$;
[d] $\nu(M{-}N_{pyridine})$

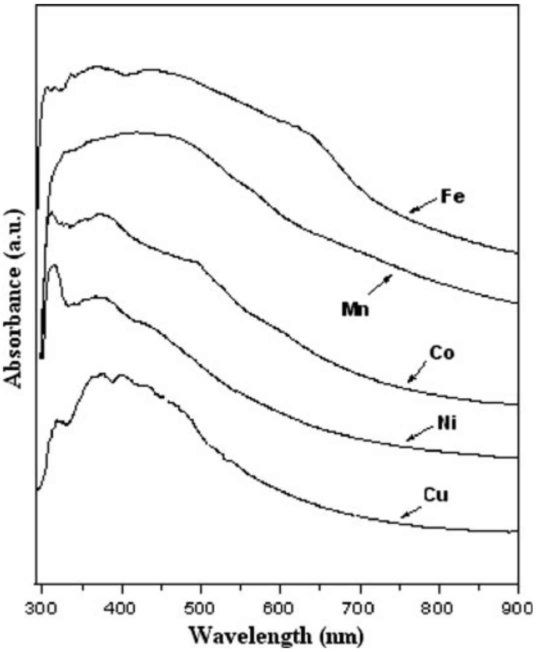


Fig. 3 DRS-UV-visible absorption spectra of polymer-anchored metal complexes

and oxidant in the solvent so that the substrates and oxidant can easily approach the active sites of the catalyst.

Effect of oxidant

In order to design the best catalytic system, the ability of different oxidants such as *tert*-butylhydroperoxide (TBHP) (70% aq.), hydrogen peroxide (H_2O_2) (30% aq.), cumene hydroperoxide, iodosyl benzene (PhIO) and molecular oxygen was examined in the oxidation of cyclohexene. In the absence of oxidant, the reaction did not proceed. As shown in Table 4, TBHP in acetonitrile medium was most efficient oxidant source to oxidize cyclohexene because of its unreactiveness in the absence of catalyst and good

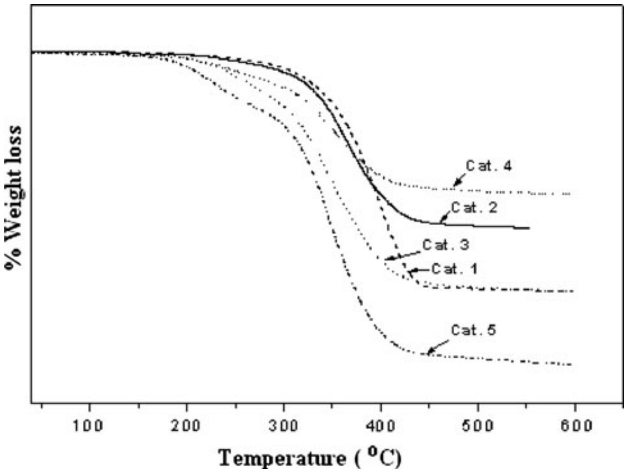
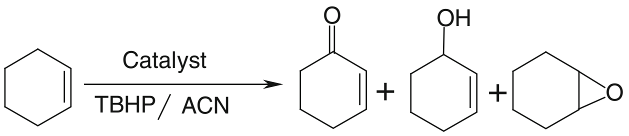


Fig. 4 Thermogravimetric weight loss plots for polymer-anchored metal complexes



Scheme 2 Various oxidation products of cyclohexene

Table 3 Effect of solvents on the catalytic oxidation of cyclohexene

Entry	Solvent	Conversion (%)				
		Cat. 1	Cat. 2	Cat. 3	Cat. 4	Cat. 5
1.	ACN	86	80	69	62	83
2.	MeOH	69	58	56	49	65
3.	DCM	48	39	26	22	40
4.	Toluene	20	16	12	07	14
5.	Benzene	07	Trace	Trace	Trace	Trace

Reaction conditions [cyclohexene] = 5 mmol; catalyst = 0.88 mmol; [TBHP] = 10 mmol; solvent = 10 mL; temperature = 60 °C; reaction time = 8 h

Conversion refers to GC & GC-MS analysis

Table 4 Effect of oxidant on the catalytic oxidation of cyclohexene

Entry	Oxidant	Conversion (%)				
		Cat. 1	Cat. 2	Cat. 3	Cat. 4	Cat. 5
1.	TBHP	86	80	69	62	83
2.	H_2O_2	54	45	32	16	43
3.	PhIO	45	34	27	12	35
4.	Cumene hydroperoxide	–	–	–	–	–
5.	Molecular O_2	14	09	Trace	Trace	16

Reaction conditions [cyclohexene] = 5 mmol; catalyst = 0.88 mmol; [oxidant] = 10 mmol; acetonitrile = 10 mL; temperature = 60 °C; reaction time = 8 h

Conversion refers to GC & GC-MS analysis

solubility in acetonitrile medium. Oxidants like H_2O_2 and PhIO were found to be less effective than TBHP and gave moderate conversion of cyclohexene. Using cumene hydroperoxide as oxidant, no conversion was obtained. In the presence of molecular oxygen, cyclohexene was oxidized but lower yield of products was obtained.

Effect of reaction temperature

The reaction temperature has a strong influence on the progress of the cyclohexene oxidation. The effect of reaction temperature on the progress of oxidation of cyclohexene was studied at different temperatures with the present catalysts. The oxidation reaction was carried out using 1:2 mmol ratio of cyclohexene-to-TBHP in acetonitrile medium for 8 h with different reaction temperatures from 40 °C to 80 °C, and results are shown in Table 5. As expected, cyclohexene conversion was increased with increasing reaction temperature, although no conversion was detected when the reaction temperature was below 40 °C. However, high temperature led to a quick decomposition of peroxide, conversely lowering down the conversion. The optimum temperature was 60 °C.

Effect of reaction time

The time dependence of the catalytic oxidation of cyclohexene was studied by performing the reaction of cyclohexene (5 mmol) with TBHP (10 mmol) in the presence of 0.88 mmol catalyst at 60 °C with constant stirring. The results are presented in Fig. 5. The reaction hardly occurred during the first 1 h, which might be the initiation period. After the initiation period, the cyclohexene conversion increased for every catalyst as reaction time was prolonged. Comparison of the results during 2–10 h exhibited in Fig. 5 showed that highest conversion of cyclohexene was obtained after 8 h and then remained stable. Selectivity of the products was not significantly changed with increasing time.

Effect of substrate-to-oxidant ratio

The substrate-to-oxidant ratio is another important parameter influencing the results of this oxidation reaction. Effect of mole ratio of cyclohexene/TBHP was investigated in the range of 1.0–3.0, and the results are given in Table 5. A lower conversion of cyclohexene was observed with 1:1 mol ratio of cyclohexene/TBHP. Increasing the substrate-to-oxidant molar ratio from 1:1 to 1:2, the conversion of cyclohexene increased markedly. Further increasing this ratio to 1:3 hardly affected the conversion but decreased the selectivity for 2-cyclohexene-1-one. Based on the results, the mole ratio of 1:2 was chosen as the optimal ratio of cyclohexene/TBHP.

Table 5 Effect of reaction temperature, substrate-to-oxidant ratio and catalyst concentration on the catalytic oxidation of cyclohexene

Reaction parameters	Conversion (%)				
	Cat. 1	Cat. 2	Cat. 3	Cat. 4	Cat. 5
Temperature (°C)					
40	49	43	32	29	47
60	86	80	69	62	83
80	80	75	62	58	76
Substrate: oxidant					
1:1	37	32	23	18	24
1:2	86	80	69	62	83
1:3	86	80	69	62	83
Catalyst concentration (g)					
0.02	52	44	40	31	43
0.04	86	80	69	62	83
0.06	86	80	69	62	83

Conversion refers to GC & GC-MS analysis

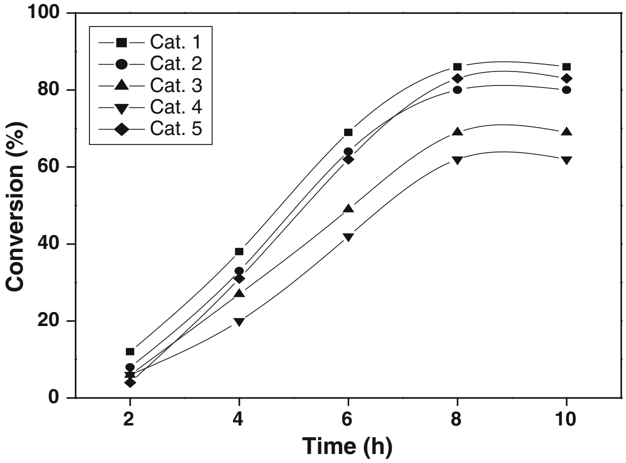


Fig. 5 Effect of reaction time on oxidation of cyclohexene using present catalysts. Reaction condition: cyclohexene (5 mmol), acetonitrile (10 mL), TBHP (10 mmol), catalyst (0.88 mmol) and temp. = 60 °C

Effect of amount of catalyst

The influence of amount of catalyst on the oxidation of cyclohexene was carried out over the range 0.4–1.4 mmol, while the cyclohexene conc. (5 mmol), TBHP conc. (10 mmol), temp (60 °C) and time (8 h) were kept constant. The effect of amount of catalyst on the oxidation of cyclohexene as a function of time is illustrated in Table 5. A control experiment was also carried out with cyclohexene as a representative case, in the presence of TBHP, without the addition of catalyst. It was observed that in the absence of any added catalyst, very poor conversion of cyclohexene (7%) was obtained. At low catalyst concentration (0.44 mmol catalyst), moderate conversion of cyclohexene was obtained. With the increase in catalyst amount from 0.44 to 0.88 mmol, the conversion of cyclohexene increased. This may be due to the availability of more active sites of the catalyst that favors the accessibility of larger number of molecules of substrates and oxidant to the catalyst. Cyclohexene conversion remained almost constant upon further increase in catalyst amount to 1.32 mmol.

Thus, the optimum reaction conditions for the oxidation of cyclohexene were as follows: cyclohexene (5 mmol), 70% aqueous TBHP (10 mmol), catalyst (0.88 mmol), ACN (10 mL) time (8 h) and temperature (60 °C). Among these catalysts, Cat 1 was found to be the most active, while the least active catalyst was Cat. 4. The following order of catalytic activities toward oxidation of cyclohexene was obtained for the complexes: Cat. 1 > Cat. 5 > Cat. 2 > Cat. 3 > Cat. 4. The selectivity and activity results of these catalysts on the oxidation of cyclohexene are given in Table 6. These catalysts were also tested for the catalytic oxidation of other olefins and alcohols under optimized reaction conditions, and the obtained results are summarized in Table 6. Results of Table 6 also show the catalytic activity of the neat metal chlorides. Comparing the catalytic activity between neat and polymer-anchored complexes proves that polymer-supported catalyst gave higher conversion of cyclohexene than their corresponding metal chlorides. The higher activity of supported complexes is because of site isolation of the complexes. Many efficient heterogeneous catalysts have been reported for the oxidation of cyclohexene with TBHP [36–38]. The results are summarized in Table 7. Comparison of these catalysts with previously reported systems reveals that the present systems give better yields than other catalysts.

Heterogeneity test

An important criterion in the commercial applications of transition metal catalysts is to obtain metal-free end products, since metal contamination is of great concern for food and pharmaceutical industries. The heterogeneity of the catalyst was verified by performing the typical hot-filtration experiment. Hot-filtration test was performed in the oxidation reaction of cyclohexene with Cat. 1. During catalytic reaction, the solid catalyst was separated from the reaction mixture by filtration after 4 h and the determined conversion was 38%. The reaction was carried out for a further 6 h. The gas chromatographic analysis showed no noticeable increment in the conversion. This confirms that the reaction did not proceed upon the removal of the solid catalyst. Further, atomic absorption spectrometric analysis of the liquid phase of the reaction mixtures collected by filtration confirms that Cu is absent in the filtrate. Metal content of the catalyst also remained unaltered, indicating no leaching of the metal from the polymer support. These results suggest that the metal is not being leached out from the catalyst during catalytic reactions.

Catalyst reuse and stability

To assess long-term stability and reusability of the polymer-anchored metal complexes, recycling experiments were carried out for oxidation of cyclohexene. After each experiment, the catalyst was separated by simple filtration, washed, dried under vacuum and then subjected to the next run under the same experimental 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 product were comparable with those of the original run. From the Table 8, it is seen that after four recycles, there is a small decrease in the conversion. Selectivity of the products remained almost the same after the fourth recycle. The nature of the recovered catalyst has been followed by IR and UV–vis spectra. The results indicated that the catalysts after reusing several times, showed no change in their IR and UV–vis spectra. From

Table 6 Oxidation of various substrates with polymer-anchored Schiff base metal complexes

Entry	Substrates	Catalyst	Conversion^a (%)	Selectivity (%)		TOF (h^{-1})
1.	Cyclohexene			2-cyclohexene-1-one	2-cyclohexene-1-ol	
		Cat. 1	86	77	18	610.8
		Cat. 2	80	74	24	568.2
		Cat. 3	69	63	21	490.1
		Cat. 4	62	60	27	369.3
		Cat. 5	83	79	14	589.5
2.	1-hexene			1-hexanone		
		Cat. 1	65	100		461.6
		Cat. 2	53	100		411.9
		Cat. 3	42	100		298.3
		Cat. 4	27	100		191.7
		Cat. 5	55	100		390.6
3.	Styrene			Benzaldehyde	Styrene epoxide	
		Cat. 1	79	79	21	561.1
		Cat. 2	70	78	28	497.2
		Cat. 3	53	68	32	376.4
		Cat. 4	47	70	30	333.8
		Cat. 5	73	75	25	518.5
4.	Benzylalcohol			Benzaldehyde		
		Cat. 1	83	100		589.5
		Cat. 2	75	100		532.7
		Cat. 3	66	100		468.7
		Cat. 4	54	100		383.5
		Cat. 5	73	100		518.5
5.	Ethylbenzene			Benzaldehyde	Others	
		Cat. 1	72	84	16	511.4
		Cat. 2	67	80	20	475.8
		Cat. 3	54	82	18	383.5
		Cat. 4	32	80	20	227.3
		Cat. 5	68	86	14	483.0
6.	Cyclohexene			2-cyclohexene-1-one	2-cyclohexene-1-ol	
		$CuCl_2^b$	46	57	31	95.8
		$CoCl_2^b$	34	63	35	70.8
		$NiCl_2^b$	20	50	36	41.7
		$MnCl_2^b$	17	59	40	35.4
		$FeCl_3^b$	44	60	32	91.7

Reaction conditions [substrate] = 5 mmol; catalyst = 0.88 mmol; [TBHP] = 10 mmol; acetonitrile = 10 mL; Temperature = 60 °C; reaction time = 8 h

[a] Conversion refers to GC & GC-MS analysis

[b] Catalyst amount = 3.0 mmol

Turn over frequency (TOF) = moles of substrate converted per mole of metal per hour

these results, we may conclude that these catalysts remain unaltered after use in the reaction.

Conclusion

Polymer-anchored Schiff base complexes of Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) have been synthesized and characterized by different analytical and spectroscopic techniques. These complexes showed high catalytic activity in the oxidation of olefins and alcohols. Under optimized reaction conditions, oxidation of cyclohexene gave three major products namely 2-cyclohexene-1-one, 2-cyclohexene-1-ol and cyclohexene epoxide and the percentage of conversion of cyclohexene varied in the order:

Table 7 Comparison of the catalytic activity of present catalytic systems with other reported systems toward oxidation of cyclohexene

Catalyst	Conversions (%)	Reaction conditions	Reference
Cat. 1	86	ACN, TBHP, 60 °C, 8 h	Present
Cat. 2	80		
Cat. 3	69		
Cat. 4	62		
Cat. 5	83		
[Mn(SAH)H_2O]-Al_2O_3	44.7	ACN, TBHP, reflux, 8 h	Salavati-Niasari and Amiri [36]
[Co(SAH)H_2O]-Al_2O_3	36.7		
[Ni (SAH)H_2O]-Al_2O_3	28.9		
[Cu(SAH)H_2O]-Al_2O_3	34.5		
α-TiCuAs	4.36	ACN, TBHP, 80 °C, 4 h	Khare and Shrivastava [37]
α-TiCoAs	5.17		
α-TiMnAs	18.65		
α-TiFeAs	11.90		
Cu-S-AmSiO_2	32.4	ACN, TBHP, 323 K, 12 h	Karandikar et al. [38]
Cu-S-AM(PS)	57.4		
Co-S-AmSiO_2	38.4		
Co-S-AM(PS)	61.3		

Table 8 Activity of the regenerated catalyst

Catalyst	Cycle	Cyclohexene conversion (%)	Product selectivity (%)	
			2-cyclohexene-1-one	2-cyclohexene-1-ol
Cat. 1	1	86	77	18
	2	85	77	18
	3	85	77	18
	4	83	78	16
Cat. 2	1	80	74	24
	2	79	74	24
	3	78	73	24
	4	78	74	24
Cat. 3	1	69	63	21
	2	67	63	21
	3	65	63	21
	4	65	63	21
Cat. 4	1	62	60	27
	2	62	59	28
	3	60	57	26
	4	60	57	26
Cat. 5	1	83	79	14
	2	83	77	13
	3	82	79	14
	4	81	79	14

Reaction conditions [cyclohexene] = 5 mmol; catalyst = 0.88 mmol; [TBHP] = 10 mmol; acetonitrile = 10 mL; Temperature = 60 °C; reaction time = 8 h

Conversion refers to GC & GC-MS analysis

Cat. 1 > Cat. 5 > Cat. 2 > Cat. 3 > Cat. 4. These supported catalysts are obtained by a simple, facile and cheap synthesis methodology. The main advantages of the present catalysts are ready accessibility, high product yield, robustness, high thermal stability and applicability for a variety of substrates. These catalysts are reused several times without appreciable decrease in their initial activities. All these facts allow us to view them as prospective heterogeneous catalysts for practical applications.

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