

Selective Oxidation of Olefins and Aromatic Alcohols with *tert*-Butylhydroperoxide Catalyzed by Polymer-Anchored Transition-Metal Complexes

S. M. Islam,¹ Anupam Singha Roy,¹ Paramita Mondal,¹ Sanchita Mondal,¹ Manir Mubarak,¹ Dildar Hossain,¹ Saikat Sarkar²

¹Department of Chemistry, University of Kalyani, Kalyani, Nadia, West Bengal 741235, India

²Department of Chemistry, Santipur College, Santipur, West Bengal 741404, India

Received 12 April 2010; accepted 25 July 2010

DOI 10.1002/app.33104

Published online 10 January 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Three polymer-anchored metal complexes (Co, Cu, and Pd) were synthesized and characterized. The catalytic performance of these complexes was tested for the oxidation of olefins and aromatic alcohols. These complexes showed excellent catalytic activity and high selectivity. These complexes selectively gave epoxides and aldehydes from olefins and alcohols, respectively. Individually, the effect of various solvents, oxidants, substrate oxidant molar ratios, temperatures, and catalyst amounts for the oxidation of cyclohexene and benzyl alcohol were

studied. Under optimized reaction conditions, 96, 81, and 71% conversions of cyclohexene and 86, 79, and 73% conversions of benzyl alcohol were obtained with Co(II), Cu(II), and Pd(II) catalysts, respectively. The catalytic results reveal that these complexes could be recycled more than five times without much loss in activity. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2743–2753, 2011

Key words: catalysts; polystyrene; recycling; supports; transition metal chemistry

INTRODUCTION

Homogeneous catalysis has been practiced for a very long time in large-scale oxidation reactions.¹ However, these homogeneous catalysts face the problem of separation from the reaction mixture and reuse; they very often decompose during the catalytic reaction. A homogeneous complex catalyst can be recovered and reused if it is heterogenized by support on an insoluble support. A variety of supports have been tested, including inorganic carriers, such as molecular sieves,² silica,³ zeolites,⁴ and clays⁵ and polymers⁶ and resins.⁷ In recent years, chloromethylated polystyrene crosslinked with divinylbenzene has been one of the most widely used macromolecular supports for the immobilization of homogeneous catalysts.^{8–11} The activity and selectivity of heterogeneous metal complexes were controlled by polymeric supports.^{12,13} The heteroge-

nization or immobilization of homogeneous complexes on polymeric supports has been developed as a promising strategy for combining the advantages of homogeneous and heterogeneous catalysts because of their easy separation from the products by filtration and their possibility of recycling by continuous operation.¹⁴ Transition-metal complexes of Mn(III), Fe(III), Cu(II), and Co(II) with polymer-supported ligands (N₂O₂ donor set) have been shown to be active catalysts for the oxidation of alkane/alkene in the presences of hydrogen peroxide (H₂O₂), PhIO, *tert*-butylhydroperoxide (TBHP), NaIO₄, and so on as oxidants.^{15–18} Apart from N₂O₂ donor ligands, polymeric supports with coordinating ligands, such as β -diketones (O,O),¹⁹ dipyriddyamine (N,N),²⁰ and diphosphine (P,P),²¹ have frequently been used to form metal complexes for catalytic applications. The chemical modification of a polymer incorporating a bifunctional ligand such as an N,O donor, has, however, received less attention.

The oxidation of olefins is a very useful reaction in industrial organic synthesis. The selective and efficient epoxidation reaction to obtain epoxides has also become very important because the epoxides are versatile intermediates in the organic synthesis of fine chemicals and pharmaceuticals.²² Among the various oxidation products of cyclohexene, cyclohexene epoxide is a highly reactive and selective organic intermediate widely used in the synthesis of enantioselective drugs, epoxy paints, and rubber promoters. Styrene oxide, an oxidation product of styrene, is

Correspondence to: S. M. Islam (manir65@rediffmail.com).

Contract grant sponsor: Department of Science and Technology (to S.M.I.)

Contract grant sponsor: Council of Scientific and Industrial Research (to S.M.I.)

Contract grant sponsor: University Grants Commission (to S.M.I.)

Contract grant sponsor: Eastern Regional Office of the University Grants Commission (to S.S.).

an important intermediate in organic synthesis and in the manufacture of the perfumery chemical, phenylethyl alcohol. 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. However, despite this intensive research effort, alcohol oxidation processes are still far from ideal from an environmental point of view and require more improvement. In particular, the oxidation of benzyl alcohol to benzaldehyde is an important organic transformation. Benzaldehyde is a very valuable chemical, which has applications in the perfumeries, pharmaceuticals, dyestuffs, and agrochemicals.^{23,24} It is traditionally produced by the hydrolysis of benzal chloride and the oxidation of toluene.^{25,26} However, benzaldehyde produced from the hydrolysis of benzal chloride often contains traces of chlorine impurities. The widely developed reaction for providing chlorine-free benzaldehyde is the catalytic liquid-phase selective oxidation of benzyl alcohol to benzaldehyde. Traditional methods based on the use of stoichiometric amounts of reagents, mainly heavy-metal salts in high oxidation states (oxidation of alcohols) and peracids (oxidation of alkenes), are useful tools for laboratory-scale preparation but not in industrial applications where serious problems related to the disposal of undesired byproducts represent a strong drawback. Hence, the preparation of such intermediates with a safer and cleaner oxidizing agent and a more active/selective, easily separable, and reusable catalyst is of great practical importance.^{27,28}

In this study, a polymer-anchored ligand was synthesized. Subsequently, it was coordinated with the metals Co(II), Cu(II), and Pd(II) to achieve complex catalysts, and these were characterized. The catalytic potential of these complexes was tested in the liquid-phase oxidation of olefins and aromatic alcohols under mild reaction conditions with TBHP as an oxidant. The effects of the molar ratio of oxidant to substrate, catalyst amount, temperature, and solvent were studied. It was observed that the catalyst containing cobalt metal showed excellent catalytic activity for the oxidation reaction. These polymer-anchored catalysts could be reused more than five times without any significant loss in their activities.

EXPERIMENTAL

Materials and equipment

Analytical-grade reagents and freshly distilled solvents were used throughout the experiment. Liquid substrates were predistilled and dried by an appropriate molecular sieve. Distillation and purification of the solvents and substrates were done by stand-

ard procedures.²⁹ Chloromethylated poly(styrene-divinyl benzene), olefins, aromatic alcohols, and anthranilic acid were supplied by Sigma-Aldrich Chemicals Co. (St. Louis, MO). Chloro salts of Pd(II), Cu(II), and Co(II) ions were received from Merck (Darmstadt, Germany) and were used without further purification.

The morphologies of the polymer-anchored ligand and complexes were analyzed with scanning electron microscopy (SEM; EVO40, Zeiss, England) equipped with an energy-dispersive X-ray spectroscopy (EDX) instrument. The thermal stability of the immobilized catalysts was determined with a Mettler-Toledo 851 thermogravimetric analysis (TGA)/simultaneous differential thermal analysis instrument. Fourier transform infrared (FTIR) spectra of the samples were recorded on a PerkinElmer FTIR 783 spectrophotometer (PerkinElmer, Waltham, Massachusetts) with KBr pellets. Diffuse reflectance ultraviolet-visible (UV-vis) spectra were taken with a Shimadzu UV-2401PC doubled-beam spectrophotometer (Shimadzu, Japan) with an integrating sphere attachment for solid samples. A PerkinElmer 2400C elemental analyzer was used to collect micro-analytical data (C, H, and N). The magnetic moment of the complexes was determined at room temperature with the Guoy method. The metal loadings in the polymer were analyzed with a Varian AA240 atomic absorption spectrophotometer (Varian, Palo Alto, CA).

Synthesis of the catalysts

The outline for the preparation of the polymer-anchored metal(II) [M(II)] complexes is given in Scheme 1.

Synthesis of the polymer-anchored ligand

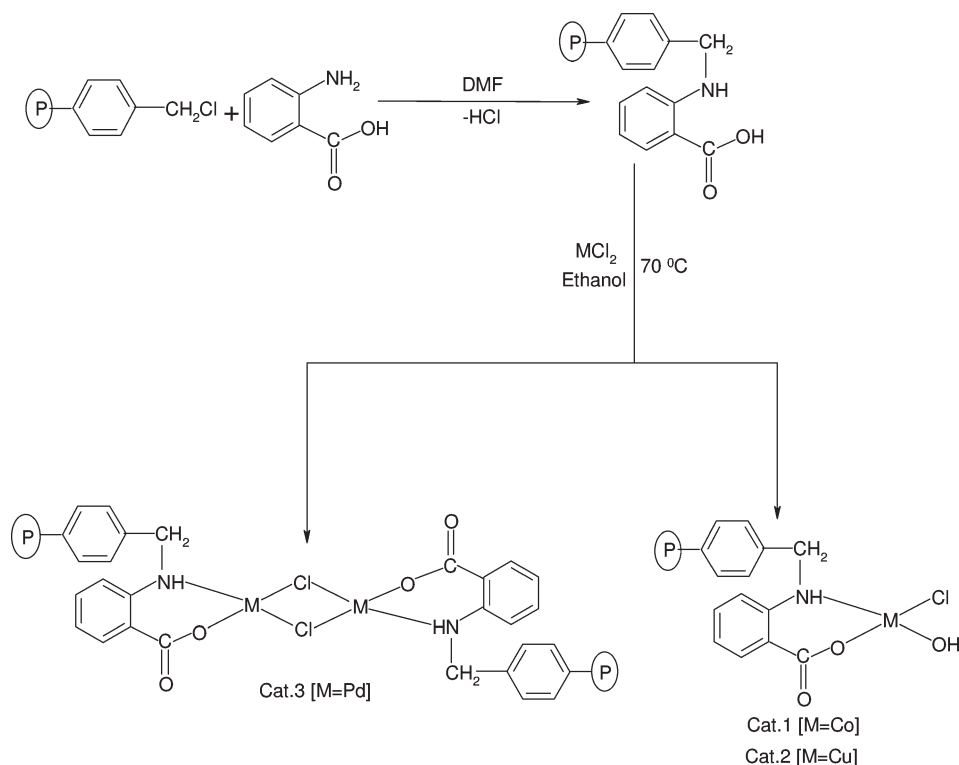
The polymer-anchored ligand was prepared according to the literature.³⁰ To 1.00 g of chloromethylated beads suspended in 50 mL of dimethylformamide (DMF) was added 0.5 g of anthranilic acid. This was stirred for 20 h, filtered, and washed with 200 mL of absolute ethanol.

2: C, 74.90%; H, 5.87%; N, 5.48%.

where **2** indicates polymer anchored ligand which synthesize in Scheme 1 (step 1).

Loading of metal ions onto the polymer-anchored ligand

The loading of metal ions onto the polymeric support was carried out as follows: the polymer-anchored ligand (1.00 g) was stirred for 24 h with 0.10 g of metal salt in 10 mL of absolute ethanol at 70°C. At the end of this reaction, the metal-loaded polymer was filtered; washed thoroughly with ethanol, dioxane, and



Scheme 1 Synthesis of the polymer-anchored metal complexes.

methanol to ensure the removal of any unreacted metal ions; and dried *in vacuo* for 6 h at 90°C.

Catalyst 1 (Cat. 1): C, 52.58%; H, 4.31%; N, 3.79%; Cl, 9.71%; Co, 3.72%.

Catalyst 2 (Cat. 2): C, 51.96%; H, 4.28%; N, 3.71%; Cl, 9.59%; Cu, 4.77%.

Catalyst 3 (Cat. 3): C, 48.75%; H, 3.52%; N, 3.43%; Cl, 8.92%; Pd, 5.28%.

Catalytic oxidation

A typical experimental procedure for the oxidation reaction with polymer-anchored metal catalysts is described as follows: the catalyst (50 mg) was placed in a two neck round-bottom flask fitted with a water condenser and placed in a thermostatted oil bath under vigorous stirring. The substrates (5 mmol) were placed in 10 mL of acetonitrile (ACN) for different sets of reactions, to which 10 mmol of oxidant was added. Then, the reaction mixture was stirred magnetically at different temperatures. At the end of specified time, the contents were analyzed by Varian 3400 gas chromatograph equipped with a 30-m CP-SIL8CB capillary column and a flame ionization detector. The peak position of various reaction products were compared and matched with the retention times of authentic samples. The identity of the products was also confirmed with an Agilent gas chromatography (GC)/mass spectrometry (MS) apparatus (Agilent, Santa Clara, CA).

RESULTS AND DISCUSSION

Characterization of the polymer-anchored metal complexes

Because of the insolubilities of the polymer-anchored metal complexes in all common organic solvents, their structural investigation was limited to their physicochemical properties, chemical analysis, SEM, TGA, IR, and UV-vis spectral data. The elemental analyses of the ligand and complexes supported the formulation of the complexes. The metal contents of Cat. 1, Cat. 2, and Cat. 3, determined by atomic absorption spectroscopy, suggested 3.72% (w/w) Co, 4.77% (w/w) Cu, and 5.28% (w/w) Pd in the immobilized metal complexes, respectively.

Field-emission scanning electron microscopy (FESEM) micrographs for single beads of polymer-anchored ligand and complexes were recorded to understand the morphological changes occurring in the polystyrene beads at various stages of the synthesis. In Figure 1, SEM images of the polymer-anchored ligand and the immobilized cobalt, copper, and palladium complexes on the functionalized polymer are shown. The pure polystyrene bead had a smooth surface (not shown). The introduction of ligands into the polystyrene beads through covalent bonding caused the light roughening of the top layer of the polymer-anchored beads. After metal was loaded on the polymer-anchored ligand, changes in the morphology of the ligand surface were observed by

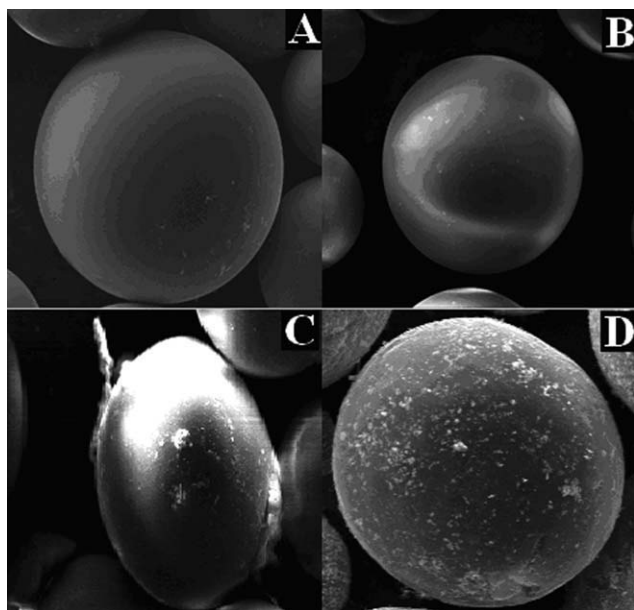


Figure 1 FESEM images of (A) the polymer-anchored ligand and (B–D) the polymer-anchored complexes of Co(II), Cu(II), and Pd(II), respectively.

SEM. As expected, the smooth and flat surface of the polymer showed slight roughening on complexation. Also, the presence of metals along with oxygen and chlorine was further proven by EDX analysis (Fig. 2), which suggested the formation of metal complexes with the polymer-anchored ligand.

TGA of the supported catalysts and the precursor, polymer-anchored anthranilic acid, was done in an air atmosphere at a heating rate of $10^{\circ}\text{C}/\text{min}$ and is shown in Figure 3. The polymer-anchored metal complexes were stable up to about 400°C , whereas the polymer-anchored ligand decomposed at 360°C (not shown in Fig. 3). After complexation of the metal ions on the polymer-anchored ligand, the thermal stability of the ligand slightly improved. The Co(II) complex decomposed at 415°C . On the other hand, the Cu(II) and Pd(II) complexes decomposed at 430 and 385°C , respectively. So, the TG profile showed that the Cu(II) complex was more stable than other two.

Various framework bondings present in the polymer-supported metal catalysts were obtained from the FTIR spectroscopy results. The sharp C–Cl peak due to the $-\text{CH}_2\text{Cl}$ group in the polymer at 1260 cm^{-1} was absent after anthranilic acid was loaded on the support.³¹ A strong band at 3455 cm^{-1} due to $-\text{NH}$ (secondary amine) vibration was observed in the polymeric support. These two IR data confirmed the loading of anthranilic acid on the polymer matrix. $\nu(\text{OH})$, $\nu(\text{C}=\text{O})$, $\nu_{\text{asym}}(\text{COO})$, and $\nu_{\text{sym}}(\text{COO})$ stretching vibrations were observed at 3448, 1705, 1589, and 1420 cm^{-1} for the polymer-anchored ligand.³² The amino acid was found to be bidentate ligands and was bound to the central metal ion through the carboxylic $-\text{OH}$ and the secondary amino group, $-\text{NH}-$. Bands at 1589 and 1422 cm^{-1}

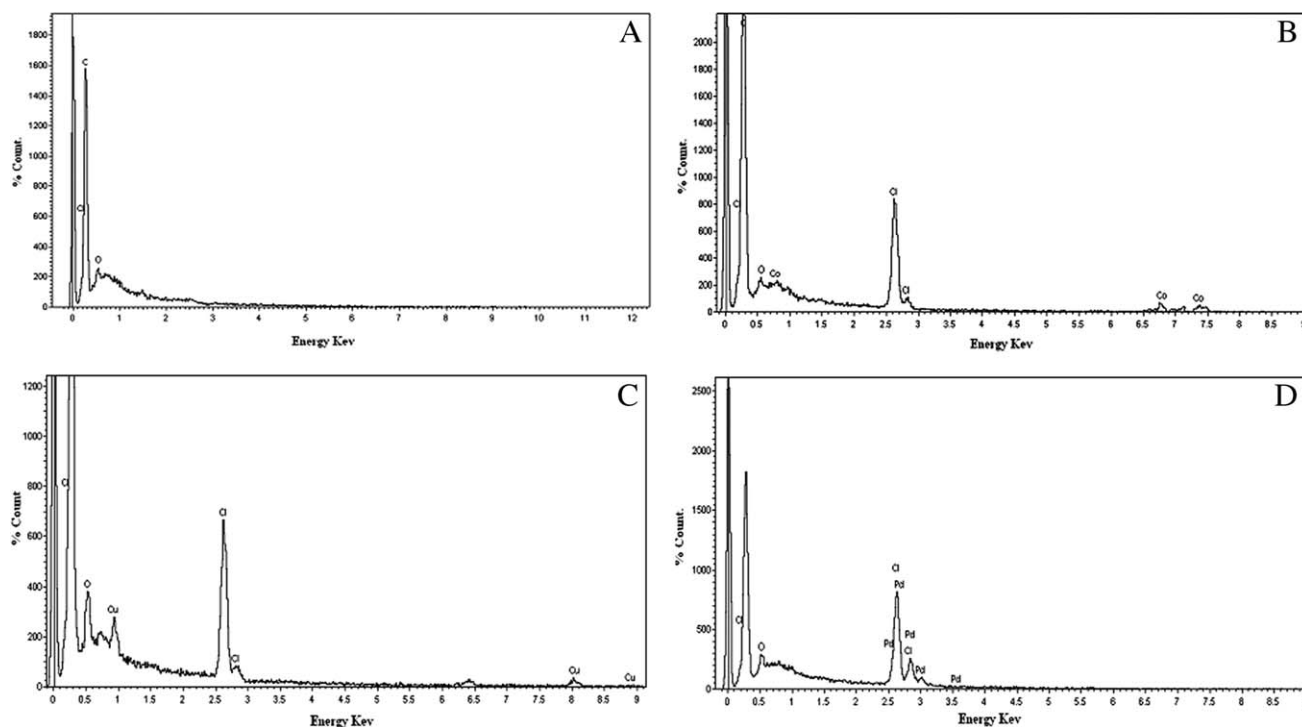


Figure 2 EDX images of (A) the polymer-anchored ligand and (B–D) the polymer-anchored complexes of Co(II), Cu(II), and Pd(II), respectively.

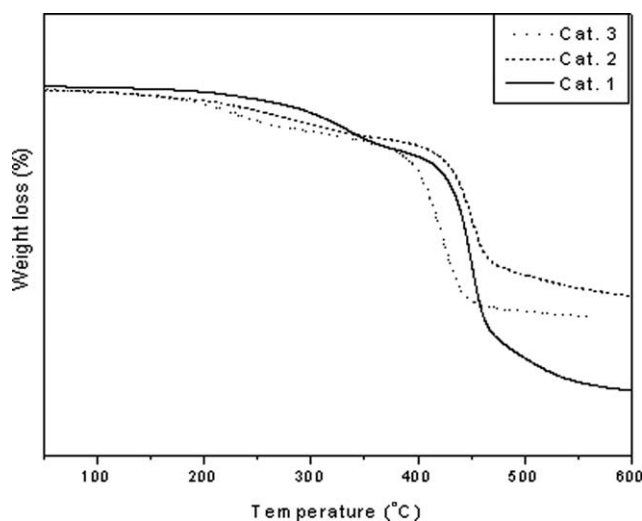


Figure 3 Thermogravimetric weight-loss plots of the polymer-anchored complexes of Co(II) (Cat. 1), Cu(II) (Cat. 2), and Pd(II) (Cat. 3).

due to $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ of the amino acids, respectively, appeared in the complexes at 1555 and 1310 cm^{-1} . The shift of these two bands suggested the involvement of the carboxylic groups of the amino acids in complex formation.^{33,34} The participation of the OH group in bonding was confirmed from the shift in the position of the δOH of the free ligand (1406 cm^{-1}) by 8–10 cm^{-1} in the spectra of the complexes. Also, it was evidenced from the phenolic C–O stretch band (1242 cm^{-1}), which shifted into the lower range.³⁵ The decrease in the N–H stretching frequency of the secondary amine group in the complexes indicated that the N of the amino group may have been coordinated to the metals.³⁶ In addition, the interactions of metal ions with ligand showed new absorption bands at 532, 548, and 455 cm^{-1} with the polymer-anchored ligand in Cat. 1–3, respectively; this was due to the formation of M–N bonds between the metal ions and the polymer-anchored ligand.^{37,38} The complexation of Co(II), Cu(II), and Pd(II) metals also resulted in absorption bands at 647, 652, and 358 cm^{-1} due to the formation of metal bonds with phenolic oxygen (M–O).^{37,39} Cat. 1 and Cat. 2 showed $\nu_{\text{M-Cl}}$ characteristic frequencies at 330 and 315 cm^{-1} , respectively.⁴⁰ The far IR spectrum of Cat. 3 exhibited a broad intense band around 332 cm^{-1} ; this was assigned to $\nu_{\text{Pd-Cl}_{\text{bridge}}}$.⁴¹

Magnetic moment measurements were carried out in the solid state at room temperature. The room-temperature magnetic moment of the polymeric Pd(II) complex was diamagnetic because of the spin-paired d^8 system.⁴² This diamagnetic nature supported the formation of a low-spin, square-planar geometry around Pd(II). On the other hand, the

polymeric Co(II) and Cu(II) complexes were paramagnetic in nature. The Cu(II) complex showed a magnetic moment value of 1.91 BM,⁴³ a value close to the spin-only value of 1.73 BM expected for a spin ($S = 1/2$) system, whereas the magnetic moment value of the Co(II) complex was 2.6 BM; this generally arises from one unpaired electron and an apparently large orbital contribution and is also diagnostic of coordination geometry around a low-spin, square-planar Co(II) ion.⁴⁴

The electronic spectra of all of the polymeric M(II) catalysts (Fig. 4) were recorded in diffuse reflectance spectrum mode as $\text{MgCO}_3/\text{BaSO}_4$ discs because of their solubility limitations in common organic solvents. The low-spin Pd(II) complex may exhibit three spin-allowed $d-d$ transitions from lower lying d orbitals to higher empty $d_x^2-d_y^2$ orbitals. The bands were observed at 315–340, 360–385, and 425–485 nm, which were designated as the $^1A_{1g} \rightarrow ^1E_g$, $^1A_{1g} \rightarrow ^1B_{1g}$, and $^1A_{1g} \rightarrow ^1A_{2g}$ transitions, respectively.^{45,46} The reflectance spectrum of the Cu(II) catalyst showed a broad band centered at 440 nm, which was assigned to the charge-transfer transition, whereas the shoulder around 600 nm was attributed to the $^2B_{1g} \rightarrow ^2A_{1g}$ transition in a square-planar stereochemistry.⁴⁵ The electronic spectrum of the Co(II) complex showed a sharp peak around 400; this was attributed to the $\pi-\pi^*$ transition, whereas the absorption bands in the region 620–640 nm were assigned to the $^2A_{1g} \rightarrow ^2B_{1g}$ transition in the square ligand field around Co(II).⁴⁵ On the basis of these results from elemental analysis, IR spectroscopy, electronic spectra, magnetic moment measurements, and thermal analysis, the structures of the Co(II), Cu(II), and Pd(II) complexes are suggested and are given in Scheme 1.

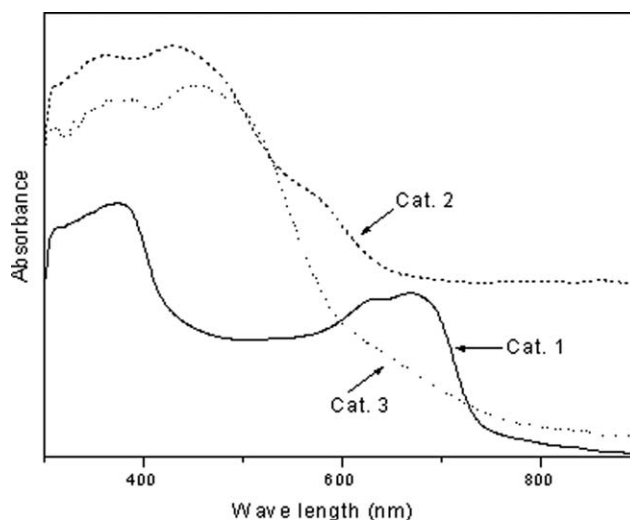
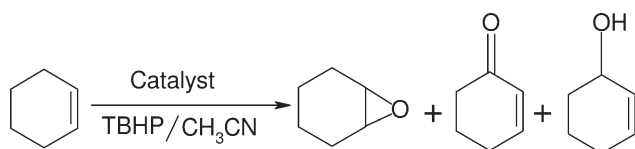


Figure 4 Diffuse reflectance spectra–UV–vis absorption spectra of the polymer-anchored complexes of Co(II) (Cat. 1), Cu(II) (Cat. 2), and Pd(II) (Cat. 3).



Scheme 2 Various oxidation products of cyclohexene.

Catalytic activity

Oxidation of olefins

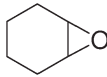
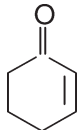
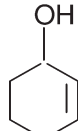
The oxidation of olefins catalyzed by polymer-anchored Co(II), Cu(II), and Pd(II) complexes with TBHP as an oxidant selectively gave epoxide. Among the polymer-anchored complexes, the Co(II) complex was taken as a representative, and among the olefins, cyclohexene was taken as a substrate. On oxidation, cyclohexene gave three oxidation products, namely, cyclohexene epoxide, 2-cyclohexene-1-ol, and 2-cyclohexene-1-one at 6 h (Scheme 2). Five different parameters, namely, the solvent, oxidant, molar ratio of TBHP to cyclohexene, amount of catalyst, and temperature of the reaction, were varied to optimize the reaction conditions for the maximum yield of epoxide.

To study the effects of the solvents, several solvents were used in the oxidation of cyclohexene (5 mmol) with TBHP (10 mmol) at 50°C, with the other parameters kept constant (Table I, entries 1–4). The conversion of cyclohexene in four solvents over the polymer-anchored Co(II) catalyst decreased in the following order: ACN (96%) > Methanol (62%) > Dichloromethane (49%) > H₂O (34%). The higher catalytic activity in ACN was due to the dielectric constant, polarity of solvent, and better solubility of the substrate and oxidant in the solvent so that the

substrates and oxidant could easily approach the active sites of the catalyst. Different oxidants were used to study the effect of the oxidant in the oxidation of cyclohexene in ACN (Table I, entries 4–7). Among H₂O₂ (30% aqueous), atmospheric O₂, TBHP (70% aqueous), and PhIO, the most active oxidant was found to be TBHP. So TBHP was used as the oxidant in the ACN medium. Cyclohexene was oxidized in the presence of molecular oxygen to give good selectivity for the epoxides, but the conversion was low. In the presence of H₂O₂, allylic oxidation products, such as 2-cyclohexene-1-ol and 2-cyclohexene-1-one, were the main products; this may have been due to the homolytic cleavage of peroxide.

The activity of the polymer-anchored Co(II) complexes in the oxidation of cyclohexene was also evaluated with three different molar ratios of cyclohexene to TBHP. For cyclohexene-to-TBHP molar ratios of 1 : 1, 1 : 2, and 1 : 3, the cyclohexene (5 mmol) and catalyst (50 mg) were placed in 10 mL of ACN, and the reaction was carried out at 50°C. As illustrated in Figure 5, the conversion of cyclohexene increased from 79 to 96% with increasing cyclohexene–TBHP ratio from 1 : 1 to 1 : 2. When this ratio was increased further to 1 : 3, the conversion was hardly affected. From these results, we concluded that the 1 : 2 ratio of cyclohexene to TBHP was sufficient for the good conversion of cyclohexene. Similarly, the effect of the catalyst amount on the conversion of cyclohexene was investigated with three different amounts, namely, 40, 50, and 60 mg of catalyst, with the other parameters kept constant. Under these reaction conditions, 40 mg of catalyst gave only 56% conversion, whereas 50 and 60 mg of catalyst showed a maximum conversion of 96%; this suggested that a large amount of catalyst was not

TABLE I
Effects of Different Solvents and Oxidants on the Oxidation of Cyclohexene with the Polymer-Anchored Co(II) Complex

Serial no.	Oxidant	Solvent	Conversion (%)	Selectivity (%)		
						
1	TBHP	Methanol	62	72	16	12
2	TBHP	Dichloromethane	49	66	21	13
3	TBHP	H ₂ O	34	59	27	14
4	TBHP	ACN	96	89	7	4
5	H ₂ O ₂	ACN	35	—	58	42
6	O ₂	ACN	17	74	16	10
7	PhIO	ACN	9	58	26	16

Reaction conditions: amount of cyclohexene = 5 mmol, amount of the oxidant = 10 mmol, volume of the solvent = 10 mL, temperature = 50°C, and time = 6 h. The yield refers to GC and GC–MS analysis.

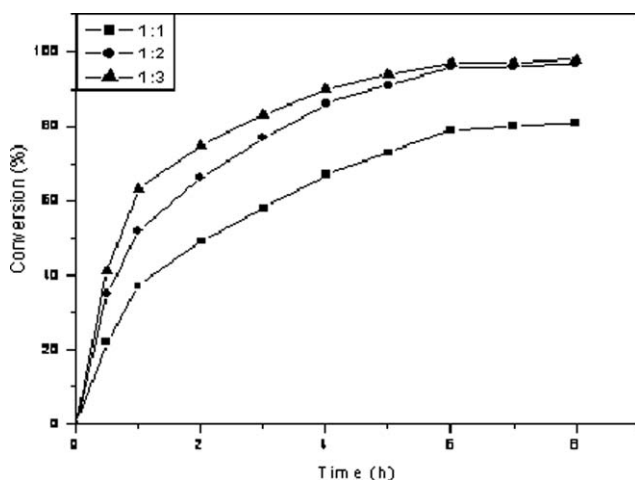


Figure 5 Effect of the cyclohexene/TBHP ratio (mmol) on the oxidation of cyclohexene as a function of time with the polymer-anchored Co(II) complex (reaction conditions: amount of cyclohexene = 5 mmol, catalyst mass = 0.05 g, volume of ACN = 10 mL, and temperature = 50°C).

needed to improve the oxidation product during the reaction (Fig. 6).

The effect of the temperature on the performance of the catalyst was studied at three different temperatures, namely, 40, 50, and 60°C, with fixed amounts of cyclohexene (5 mmol), TBHP (10 mmol), and Co(II) catalyst (50 mg) in 10 mL of ACN (Fig. 7). A maximum of 96% conversion was achieved when the reaction was carried out at 50°C. At 40°C, the conversion was low. At 60°C, the initial conversion of cyclohexene was higher than at 50°C, but when the reaction continued, the conversion of cyclohex-

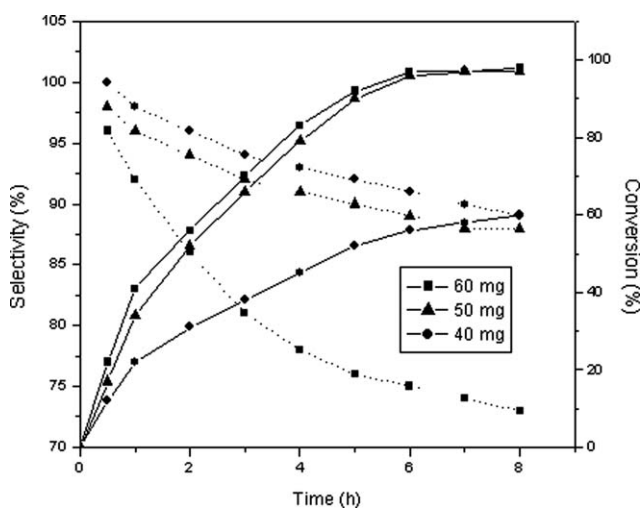


Figure 6 Effect of the amount of the catalyst on the oxidation of cyclohexene as a function of time with the polymer-anchored Co(II) complex (reaction conditions: amount of cyclohexene = 5 mmol, amount of TBHP = 10 mmol, volume of ACN = 10 mL, and temperature = 50°C): (· · ·) selectivity of cyclohexene epoxide and (—) conversion of cyclohexene.

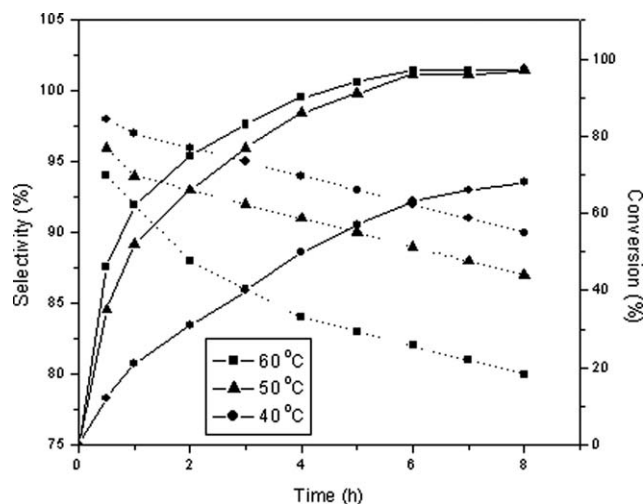


Figure 7 Effect of the temperature on the oxidation of cyclohexene as a function of time with the polymer-anchored Co(II) complex (reaction conditions: amount of cyclohexene = 5 mmol, amount of TBHP = 10 mmol, catalyst mass = 0.05 g, and volume of ACN = 10 mL): (· · ·) selectivity of cyclohexene epoxide and (—) conversion of cyclohexene.

ene was almost same as the conversion at 50°C. Therefore, 50°C was the optimum temperature, and all of the catalytic oxidation reactions of the olefins were carried out at this temperature.

Under these optimized conditions, that is, with 5 mmol of cyclohexene, 10 mmol of 70% aqueous TBHP, 50 mg of catalyst, and 10 mL of ACN at a temperature of 50°C, the polymer-anchored Co(II) catalyst was tested in the oxidation of other olefins. The polymer-anchored Cu(II) and Pd(II) catalysts were also tested in the oxidation of other olefins under the optimized reaction conditions for the Co(II) catalyst, and the obtained results are shown in Table II. The results in Table II provide information about the conversion, along with the selectivity of the various products at 6 h of reaction time. It is clear that the polymer-anchored Co(II) catalyst exhibited better catalytic activity than the others.

Oxidation of aromatic alcohols

Polymer-anchored metal complexes were examined for the oxidation of aromatic alcohols with TBHP in ACN at 6 h. As shown in Table III, three catalysts effectively catalyzed the conversion of benzyl alcohol under mild conditions, with the formation of benzaldehyde as the main product along with a trace amount of acid (Scheme 3). On the other hand, 1-phenyl ethanol selectively converted to acetophenone on oxidation with these catalysts.

The reaction conditions were optimized for the maximum conversion of benzyl alcohol by variation

TABLE II
Oxidation of Various Olefins by the Polymer-Anchored M(II) Complexes

Serial no.	Substrate	Catalyst	Conversion (%)	Selectivity (%)		
1	Cyclohexene			Cyclohexene epoxide	2-Cyclohexene-1-one	2-Cyclohexene-1-ol
		Cat. 1	96	89	7	4
		Cat. 2	81	77	14	9
2	Styrene	Cat. 3	71	69	20	11
		Cat. 1	82	85	15	—
		Cat. 2	77	80	20	—
3	Cyclooctene	Cat. 3	71	74	26	—
		Cat. 1	56	100	—	—
		Cat. 2	51	100	—	—
4	Limonene	Cat. 3	49	100	—	—
		Cat. 1	44	66	24	10
		Cat. 2	42	59	25	16
		Cat. 3	39	52	27	21

Reaction conditions: amount of the substrate = 5 mmol, amount of TBHP = 10 mmol, volume of ACN = 10 mL, temperature = 50°C, and time = 6 h. The yield refers to GC and GC-MS analysis.

of the amount of oxidant (moles of TBHP per moles of benzyl alcohol), amount of catalyst, and temperature of the reaction with Co(II) catalyst considered the representative catalyst.

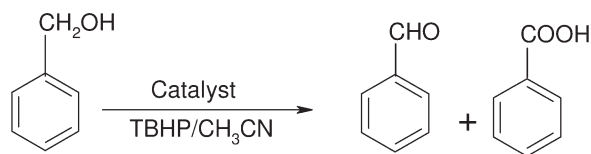
Figure 8 shows the results obtained by the variation of the molar ratios of benzyl alcohol to TBHP. Only a 54% conversion was achieved at a 1 : 1 molar ratio of benzyl alcohol to TBHP in ACN (10 mL) at 80°C after 6 h. When the molar ratio increased from 1 : 1 to 1 : 2, the conversion increased from 54 to 86%. A further increase of the TBHP concentration to 1 : 3 showed no increment in conversion. In general, the reaction temperature can have a marked effect on catalytic activity with regard to the reaction kinetics and stability of the catalytic species. The

effect of temperature on the oxidation of benzyl alcohol as a function of time for a fixed amount of benzyl alcohol (5 mmol), 70% TBHP (10 mmol), and catalyst (50 mg) in ACN (10 mL) is plotted in Figure 9. It was clear from the results that the catalyst gave better conversion at 80°C compared to lower temperatures. The effect of amount of catalyst on the oxidation of benzyl alcohol is illustrated in Figure 10. Among the three different amounts (40, 50, and 60 mg) of catalyst, at a benzyl alcohol to TBHP ratio of 1 : 2 under these reaction conditions, 50 mg of catalyst showed maximum conversion. On the other hand, 40 and 60 mg of catalyst gave 62 and 86% conversion, respectively. So, the optimized amount of catalyst for the best performance was 50 mg.

TABLE III
Oxidation of Various Aromatic Alcohols by the Polymer-Anchored M(II) Complexes

Entry	Substrate	Catalyst	Conversion (%)	Selectivity (%)	
1	Benzyl alcohol			Benzaldehyde	Benzoic acid
		Cat. 1	86	92	8
		Cat. 2	79	87	13
2	4-Methylbenzyl alcohol	Cat. 3	73	82	18
		Cat. 1	78	90	10
		Cat. 2	69	86	14
3	4-Nitrobenzyl alcohol	Cat. 3	61	80	20
		Cat. 1	80	89	11
		Cat. 2	71	84	16
4	1-Phenyl ethanol	Cat. 3	66	81	19
		Cat. 1	84	100	—
		Cat. 2	75	100	—
		Cat. 3	69	100	—

Reaction conditions: amount of the substrate = 5 mmol, amount of TBHP = 10 mmol, volume of ACN = 10 mL, temperature = 80°C, and time = 6 h. The yield refers to GC and GC-MS analysis.



Scheme 3 Various oxidation products of benzyl alcohol.

From these studies, we determined the following optimized reaction conditions for the maximum conversion of benzyl alcohol: 5 mmol of benzyl alcohol, 10 mmol of 70% TBHP, 50 mg of catalyst, and 10 mL of ACN at a temperature of 80°C . Under these conditions, polymer-anchored Co(II) gave a maximum conversion of 86% after 6 h. A conversion of 79% was obtained with the Cu(II) catalyst, whereas 73% conversion was obtained with the Pd(II) catalyst under the optimized reaction conditions. Polymer-anchored Co(II), Cu(II), and Pd(II) catalysts were also tested in the oxidation of other aromatic alcohols under optimized reaction conditions for the Co(II) catalyst, and the obtained results are shown in Table III. Table III provides information about the conversion along with the selectivity of the various products at 6 h of reaction time. It was clear that the polymer-anchored Co(II) catalyst exhibited better catalytic activity than the others. No significant improvement in the oxidation of benzyl alcohol was observed after 6 h of reaction time.

Recyclability and heterogeneity testing

The reusability of the polymer-anchored metal complexes was investigated in the oxidation of cyclohexene and benzyl alcohol. The catalysts were separated

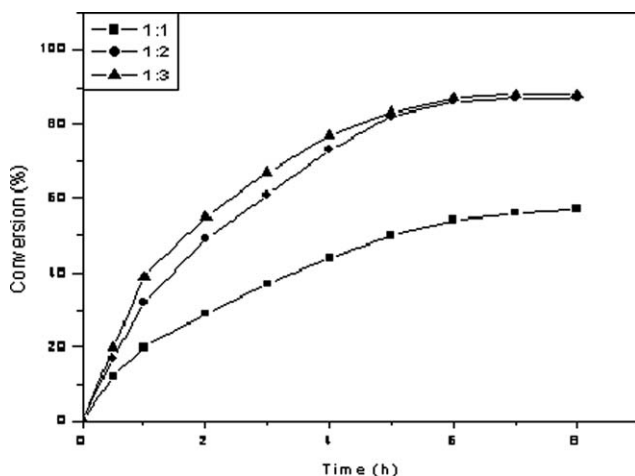


Figure 8 Effect of the benzyl alcohol/TBHP ratio (mmol) on the oxidation of benzyl alcohol as a function of time with the polymer-anchored Co(II) complex (reaction conditions: amount of benzyl alcohol = 5 mmol, catalyst mass = 0.05 g, volume of ACN = 10 mL, and temperature = 80°C).

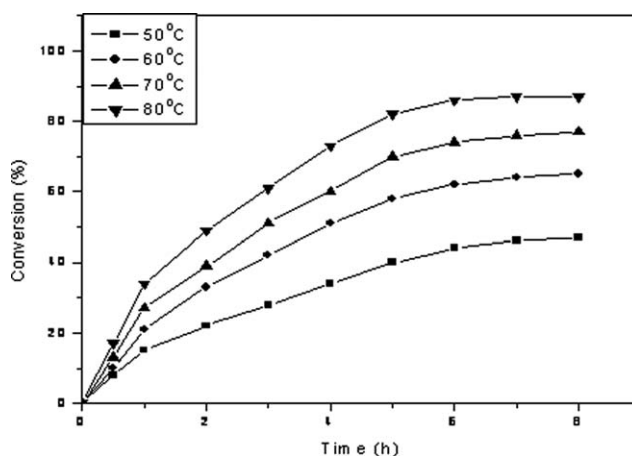


Figure 9 Effect of temperature on the oxidation of benzyl alcohol as a function of time with the polymer-anchored Co(II) complex (reaction conditions: amount of benzyl alcohol = 5 mmol, amount of TBHP = 10 mmol, catalyst mass = 0.05 g, and volume of ACN = 10 mL).

by filtration after the first catalytic run, washed with solvent, dried *in vacuo*, and then subjected to a second run under the same reaction conditions. The catalytic run was repeated with the further addition of substrates in appropriate amounts under the optimum reaction conditions, and the nature and yield of the final products were comparable to that of the original one. Table IV illustrates the reusability of these catalysts for the oxidation of cyclohexene and benzyl alcohol for five recycles. The catalytic activity did not change significantly after five repeat runs. The selectivity of the oxidation products of cyclohexene and benzyl alcohol did not change markedly in subsequent recycling runs.

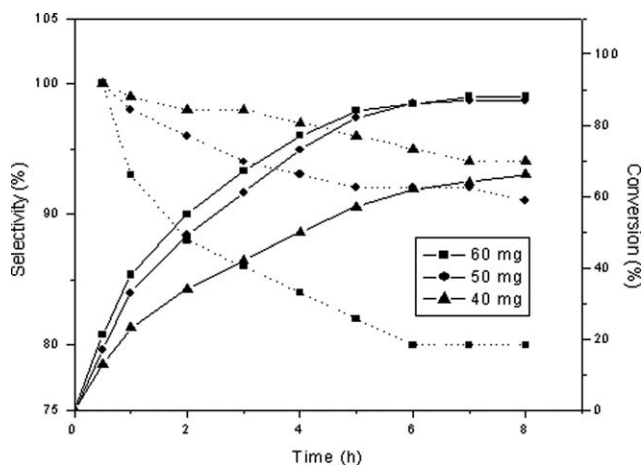
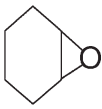
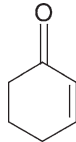
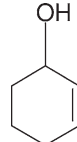
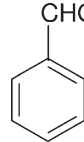
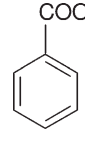


Figure 10 Effect of the amount of the catalyst on the oxidation of benzyl alcohol as a function of time with the polymer-anchored Co(II) complex (reaction conditions: amount of benzyl alcohol = 5 mmol, amount of TBHP = 10 mmol, volume of ACN = 10 mL, and temperature = 80°C): (· · ·) selectivity of benzaldehyde and (—) conversion of benzyl alcohol.

TABLE IV
Recycling Activity of the Polymer-Anchored M(II) Complexes Toward the Catalytic Oxidation of Cyclohexene and Benzyl Alcohol

Recycle no.	Catalyst	Conversion (%)	Cyclohexene			Conversion (%)	Benzyl alcohol	
			Selectivity (%)				Selectivity (%)	
								
1	Cat. 1	96	89	7	4	86	92	8
	Cat. 2	81	77	14	9	79	87	13
	Cat. 3	71	69	20	11	73	82	18
2	Cat. 1	95	88	8	4	85	92	8
	Cat. 2	80	76	15	9	77	86	14
	Cat. 3	69	67	21	12	72	81	19
3	Cat. 1	93	87	8	5	83	92	8
	Cat. 2	79	75	16	9	76	87	13
	Cat. 3	68	67	22	11	70	82	18
4	Cat. 1	92	87	9	4	83	91	9
	Cat. 2	78	74	16	10	75	86	14
	Cat. 3	67	66	23	11	69	82	18
5	Cat. 1	92	85	10	5	82	91	9
	Cat. 2	77	72	17	11	74	86	14
	Cat. 3	67	65	23	12	68	81	19

Reaction conditions: amount of the substrate = 5 mmol, amount of TBHP = 10 mmol, volume of ACN = 10 mL, temperature = 50°C for cyclohexene and 80°C for benzyl alcohol, and time = 6 h. The yield refers to GC and GC-MS analysis.

To check for the leaching of metals into the solution during the reaction, a cyclohexene oxidation experiment was carried out under the optimum reaction conditions. The reaction was stopped after the reaction proceeded for 3 h. The separated filtrate was allowed to react for another 3 h under the same reaction conditions, but no further increase in the conversion was observed in GC analyses. UV-vis spectroscopy was also used to determine the stability of these heterogeneous catalysts. The UV-vis spectra of the reaction solution, in the first run, did not show any absorption peaks characteristic of metals; this indicated that the leaching of metals did not take place during the course of the oxidation reaction. These results suggest that these catalysts were heterogeneous in nature.

CONCLUSIONS

Polymer-anchored Co(II), Cu(II), and Pd(II) catalysts, with potential catalytic activities for the oxidation of olefins and aromatic alcohols, were prepared and characterized. Under the optimized reaction conditions, the oxidation of the olefins selectively gave epoxides, and the oxidation of aromatic alcohols gave aldehyde at 6 h of reaction time. These cata-

lysts were air-stable, inexpensive, and mostly easy to make. The main advantages of the polymer-anchored catalysts used in this investigation were that (1) these catalysts could be used repeatedly for the oxidation of substrates of different natures without any appreciable loss of activity and (2) the isolation of the used catalyst from the product mixture encountered no difficulty. From the results, for all of the oxidation reactions, that with the polymer-anchored Co(II) catalyst was determined to be best. Leaching tests indicated that the catalytic reaction was mainly heterogeneous in nature. The reusability of this catalyst was high; it could be reused five times without significant decrease in its initial activity.

The authors thank the Department of Material Science of the Indian Association of Cultivation of Science (Kolkata, India) for providing the instrumental support.

References

- Comprehensive Coordination Chemistry; Quignard, F.; Choplin, A.; McCleverty, J.; Mayer, A.; Thomas, J., Eds.; Elsevier: London, 2004; Vol. 2, p 445.
- Zimowska, M.; Michalik-Zym, A.; Połtowicz, J.; Bazarnik, M.; Bahranowski, K.; Serwicka, E. M. *Catal Today* 2007, 124, 55.

3. Bakala, P. C.; Briot, E.; Salles, L.; Brégeault, J. M. *Appl Catal A* 2006, 300, 91.
4. Medina, J. C.; Gabriunas, N.; Páez-Mozo, E. *J Mol Catal A* 1997, 115, 233.
5. Gigante, B.; Corma, A.; García, H.; Sabater, M. J. *Catal Lett* 2000, 68, 113.
6. Mathew, T.; Padmanabhan, M.; Kuriakose, S. *J Appl Polym Sci* 1996, 59, 23.
7. Kotov, S. V.; Balbolov, E. *J Mol Catal A* 2001, 176, 41.
8. Sherrington, D. C. *Catal Today* 2000, 57, 87.
9. Antony, R.; Tembe, G. L.; Ravindranathan, M.; Ram, R. N. *J Appl Polym Sci* 2003, 90, 370.
10. Grivani, G.; Tangestaninejad, S.; Halili, A. *Inorg Chem Commun* 2007, 10, 914.
11. Maurya, M. R.; Arya, A.; Adao, P.; Pessoa, J. C. *Appl Catal A* 2008, 351, 239.
12. Chacko, A.; Mathew, B. *J Appl Polym Sci* 2003, 90, 3708.
13. Brule, E.; de Miguel, Y. R.; Hi, K. K. *Tetrahedron* 2004, 60, 5913.
14. Sherrington, D. C. *Supported Reagents and Catalysts in Chemistry*; Royal Society of Chemistry: Cambridge, England, 1998.
15. Mirkhani, V.; Moghadam, M.; Tangestaninejad, S.; Bahramian, B. *Appl Catal A* 2006, 311, 43.
16. Antony, R.; Tembe, G. L.; Ravindranathan, M.; Ram, R. N. *J Mol Catal* 2001, 171, 159.
17. Gupta, K. C.; Sutar, A. K. *J Appl Polym Sci* 2008, 108, 3927.
18. Kureshy, R. I.; Khan, N. H.; Abdi, S. H. R.; Iyer, P. *React Funct Polym* 1997, 34, 153.
19. Cauz, I.; Caze, C. *Eur Polym J* 1993, 29, 1615.
20. Kartz, M. R.; Hendicker, D. G. *Polymer* 1986, 27, 1641.
21. Sundell, M. J.; Nasman, J. H. *Chem Tech* 1993, 23, 16.
22. Yudin, A. K. *Aziridines and Epoxides in Organic Synthesis*; Wiley-VCH: Weinheim, 2006.
23. Kroschwitz, J. I.; Othmer, K. *Encyclopedia of Chemical Technology*; Wiley-Interscience: New York, 1992.
24. Ullmann, F. *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, 2003.
25. McGrath, D. V.; Grubbs, R. H.; Ziller, J. W. *J Am Chem Soc* 1991, 113, 3611.
26. Knight, D. A.; Schull, T. L. *Synth Commun* 2003, 33, 827.
27. Clark, J. H. *Green Chem* 2006, 8, 17.
28. Clark, J. H. *Acc Chem Res* 2002, 35, 791.
29. Vogel, A. I. *Text Book of Practical Organic Chemistry (Quantitative Analysis)*, 5th ed.; Longman: London, 1998.
30. Holy, N. L. *J Org Chem* 1979, 44, 239.
31. Valodkar, V. B.; Tembe, G. L.; Ravindranathan, M.; Ram, R. N.; Rama, H. S. *J Mol Catal A* 2004, 208, 21.
32. Mohamed, G. G.; Omar, M. M.; Hindy, A. H. H. *Spectrochim Acta A* 2005, 62, 1140.
33. Sandhu, G. K.; Verma, S. P. *Polyhedron* 1987, 6, 587.
34. Rao, N.; Rao, P. V.; Raju, V.; Ganorkar, M. C. *Indian J Chem A* 1985, 24, 877.
35. Zaki, Z. M.; Haggag, S. S.; Soayed, A. A. *Spectrosc Lett* 1998, 31, 757.
36. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1997.
37. Sallam, S. A.; Orabi, A. S. *Transition Met Chem* 2002, 27, 447.
38. Durig, J. R.; Layton, R.; Sink, D. W.; Mitchell, B. R. *Spectrochim Acta* 1965, 21, 1367.
39. Alexander, S.; Udayakumar, V.; Gayathri, V. *J Mol Catal A* 2009, 314, 21.
40. Gnanasoundari, V. G.; Natarajan, K. *Transition Met Chem* 2004, 29, 511.
41. Mani, R.; Mahadevan, V.; Srinivasan, M. *Br Polym J* 1990, 22, 177.
42. Sarkar, S.; Dey, K. *Spectrochim Acta A* 2005, 62, 383.
43. Iqbal, M. S.; Khurshid, S. J.; Iqbal, M. Z. *Can J Chem* 1993, 71, 629.
44. Dey, K.; Sarkar, S.; Mukhopadhyay, S.; Sarkar, S.; Biswas, S.; Bhaumik, B. B. *J Coord Chem* 2006, 59, 565.
45. Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: New York, 1986.
46. Bermejo, E.; Carballo, R.; Castineirs, A.; Dominguez, R.; Liberta, A. E.; Mossmer, C. M.; Salberg, M. M.; West, D. X. *Eur J Inorg Chem* 1999, 1999, 965.