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Synthesis of Styrene-Allylchloride Copolymer Supported Cobalt(II) Schiff Base Complex and Its Catalytic Activity

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ABSTRACT

N,N'-bis(acetylacetonato)phenylenediamine cobalt (II) Schiff base complex and its polymer bound analogue have been prepared and characterized for their structure and catalytic activity. To prepare heterogenized analogue of the cobalt (II) complex, a new crosslinked functional polymeric beads were prepared by suspension copolymerization of styrene (48.97 mmol, 5.1 g), allylchloride (48.97 mmol, 3.746 g) and divinylbenzene (1.50 mmol, 0.195 g) in the presence of azobisisobutyronitrile (9.0×10^{-4} mmol, 0.15 g) as initiator at $25 \pm 0.1^\circ\text{C}$ under inert atmosphere. The beads of variable crosslinked densities were prepared by varying the amount of divinylbenzene in a reaction mixture from 0.80–2.00 mmol. The beads prepared with 1.5 mmol of divinylbenzene contained 4.90 mmol (0.367 g) of allylchloride as found with the chlorine content in the beads. These beads have shown optimum degree of swelling (4.83%) and maximum attachment of N,N'-bis(acetylacetonato)phenylenediamine Schiff base (1.96 mmol g^{-1} of beads). These beads have also shown maximum loading of cobalt (II) ions on polymer anchored Schiff base (1.37 mmol g^{-1} of beads). The spectral and magnetic measurements have suggested a square planar structure for cobalt (II) complex both in homogeneous and heterogeneous state. The heterogenized cobalt (II) complex has shown an enhanced rate of decomposition of hydrogen peroxide with low activation energy (42.37 kJ mol^{-1}) in comparison to a homogenized complex (63.59 kJ mol^{-1}). The rate of decomposition has been found to be directly

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proportional to the concentration of hydrogen peroxide and cobalt (II) complex. A suitable rate expression has been derived for the decomposition of hydrogen peroxide.

Key Words: Allylchloride; Styrene; O-phenylenediamine; Heterogeneous catalysis; Copolymerization.

INTRODUCTION

The synthesis of a polymer supported catalyst offers several advantages over soluble homogeneous catalysts.^[1,2] In addition to retaining the activity and selectivity of homogeneous catalysts, the polymer bound catalysts offer efficient means for recovery and is amenable for scaling up the industrial processes.^[3,4] The microenvironment^[5] within the vicinity of the active sites on polymer support differs from that of the reaction in solution, and this leads to an interesting reaction rate and specificity. In polymer supported catalysts, the high loading of the catalyst is not as important because polymer support increases the fraction of the catalyst at the surface to allow more efficient use of the catalyst and minimize the likelihood of deactivation by aggregation as found with homogeneous catalysis.^[6,7] The polymer supported catalysts show a high turnover number^[8] in comparison to homogeneous catalysts and have been found to be suitable for various organic reactions.^[9–13] The polymer-supported catalysts have also shown high chemoselectivity in reduction of the aldehyde^[14] and selective hydrogenation of olefin.^[15] The efficiency of the catalyst on polymer support has been found to be dependent on the structure of the polymer. The crosslinked polymer-supports^[16] are highly suitable to provide microenvironment,^[5] than linear soluble polymers.^[17,18] The water-soluble polymer supports lack the advantages of a solid catalyst such as easy separation from the reactants and the products. Although insoluble linear polymer support^[19,20] offer advantages of easy separation and recycling of the catalyst, but they are unable to create enhanced activity of the reactants close to the active sites on the polymer. The distribution of the catalyst on polymer support contributes significantly towards the efficiency of the catalyst.^[21] In addition to polymeric supports, various inorganic supports^[22–25] have also been used but polymer supports have been found more attractive due to the flexibility of polymer chains, which provides stereospecificity between catalysts and reactants in the presence of solvents. Zeolites have also been used as shape selective supports^[26] but they show slow diffusion of reactants through molecular channels, hence are not suitable for reactions occurring in the liquid phase. In crosslinked polymer supports, the degree of crosslinking affects activity^[17,27,28] selectivity^[29–31] and regioselectivity.^[32] A greater similarity between immobilized and free species could be obtained by using suitable spacer groups^[33–35] between supports and the active sites, hence, a direct effect of support is distanced from the reaction zone to allow active sites to behave as similar as possible to its free analogue. The polymer-supported catalysts have been useful to prepare syndiotactic styrene.^[12] The ligand affinity^[36] for metal ions on polymer support also controls the activity of the catalyst on polymer support. The 1,3-diketonato complexes of the transition metal have been used as homogeneous catalysts due to their excellent coordination ability to metal ions due to enolization.^[37,38] The 1,3-diketonatotitanium complexes have also been used as efficient catalysts in polymerization of the olefins.^[39,40]

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The 1,3-diketonato complexes of titanium^[39] and zirconium^[40] have been used to prepare syndiotactic polystyrene but investigations on their catalytic activities on polymer support are rarely reported.^[41] Polystyrene anchored acetylacetonehydrazine Schiff base has been reported^[42] but no details about their catalytic activity are available. Cobalt (II) tetraphenylporphyrin complex anchored on polystyrene through imidazole has shown enhanced O₂ binding properties in comparison to solution analogue.^[43] The cobalt (II) ions supported on silica gel^[44] have been used as a catalyst for the oxidation of the allyl and benzylalcohol. The polymer bound cobalt (II) tetraarylporphyrins have been reported as a catalyst for the conversion of quadricyclane to norbornadiene.^[45–48] The polymer bound cobalt (II) Schiff base complex has shown a significant increase in catalytic activity in comparison to unsupported cobalt (II) complex.^[49] These investigations have clearly indicated that cobalt (II) complex on polymer support show different activity in comparison to free complex. Although acetylacetonato complexes of cobalt (II) ions using various alkylamines have been reported but no report on cobalt (II) complex of N,N'-bis(acetylacetonato)-phenylenediamine Schiff base on polymer support is available in the literature, hence efforts have been made to prepare polymer supported N,N'-bis(acetylacetonato)-phenylenediamine cobalt (II) complex and to compare its structural, thermal and catalytic characteristics with unbound analogue.

EXPERIMENTAL

Chemicals Used

Acetylacetonone (Loba Chemie Mumbai, India) with a boiling range of 132°C–135°C was used for synthesis without further purification. Styrene, divinylbenzene and allylchloride were reagent grade chemicals (Aldrich Chemical Company, USA) and used as received. All other chemicals used were of high purity grade reagents and used without further purification.

FTIR-Spectra

The infrared spectra of the ligand and its cobalt (II) complex were recorded on KBr pallets using a Perkin-Elmer-1600 Fourier Transform Spectrophotometer.

Electronic Spectra

Electronic spectra of the ligand and its cobalt (II) complex were recorded in dimethylformamide (DMF) using a UV-VIS 1601 PC Shimadzu Spectrophotometer.

Magnetic Measurements

Magnetic measurements of unbound and polymer bound cobalt (II) complex were made with a Gouy balance at 294K and used to determine the dipole moment (μ) and magnetic susceptibility (χ) of the complex.



Thermal Studies

The thermal behavior of the Schiff base and its cobalt (II) complex was determined by recording TG curve at a heating rate of 10°C/min under nitrogen atmosphere using a Stanton Red Croft STA-780 Thermal Analyzer (UK). The glass transition temperature (T_g) and melting point (m.p.) of the polymer support were recorded with a Stanton-Red Croft DSC-1500 differential scanning calorimeter.

Elemental Analysis

The elemental analysis of free Schiff base and its cobalt (II) complex was carried out using a Perkin-Elmer 240 C Elemental Analyzer. The analysis was used to determine the composition of the free and polymer anchored Schiff base.

Estimation of Cobalt (II) Ions Loading

The loading capacity of polymer anchored N,N'-bis (acetylacetonate)-o-phenylenediamine Schiff base was estimated by leaching the cobalt (II) ions from the polymer supported complex and assaying cobalt (II) ions concentration with a Perkin-Elmer 2100 Atomic Absorption Spectrometer at $\lambda_{\max} = 240.7$ nm.

Polymer Bead Size Measurements

The size of polymer beads obtained by suspension copolymerization of monomers was measured with scanning electron microscope (Leo-435, VP England) by mounting beads on metal stubs and vacuum coating with gold.

Molecular Weight Measurements

The molecular weight of the Schiff base and its Co (II) complex were determined with a Vapor Pressure Osmometer (Knauer K-700, Germany) using benzil as standard and benzene as solvent.

Swelling Studies

The degree of swelling of the polymer beads (%S) obtained at different concentrations of divinylbenzene was determined by soaking beads for 24 hrs in dimethylformamide (DMF) and measuring their size variation with scanning electron microscope.

Porosity

The porosity of the beads was calculated using initial weight (W_0) of the dried beads and weight (W_t) after swelling for 24 hrs in dimethylformamide (DMF) and using the following relationship. The density (d_s) of benzene was also used.

$$\text{Porosity} = \frac{(W_t - W_0)}{W_0 d_s}$$

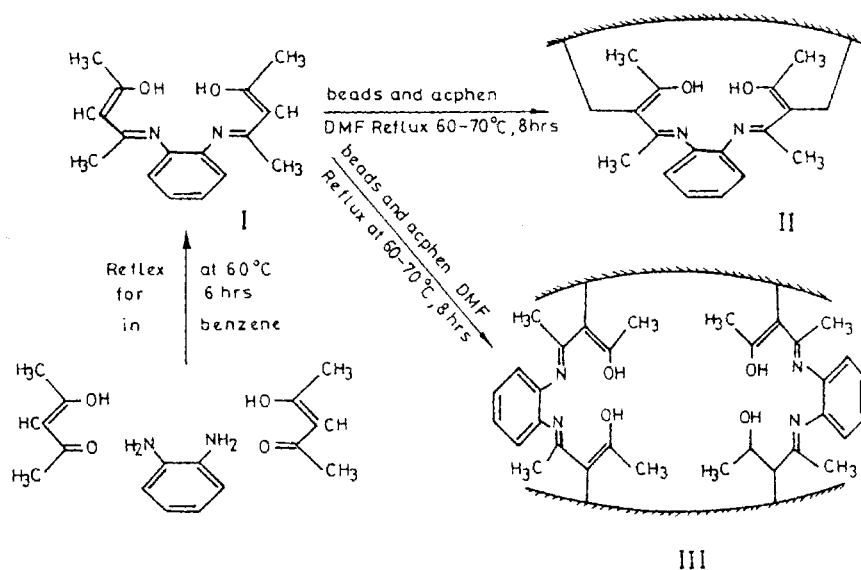
Where, d_s is the density of the benzene.

Synthesis of N,N' -bis(Acetylacetonato)-*o*-phenylenediamine Schiff Base and Its Co(II) Complex

The quadridentate N,N' -bis(acetylacetonato)-*o*-phenylenediamine Schiff base (acphen) was prepared by mixing 20 ml of methanolic solution of *o*-phenylenediamine (5 mmol, 0.54 g) in a 50 ml benzene solution of acetylacetonato (10 mmol, 1.0 g) and refluxing it at 60°C for 6 hrs. On cooling, the precipitated product (Struct. I in Sch. 1) was washed and recrystallized with methanol. The purified colorless Schiff base (Struct. I in Sch. 1) thus obtained was dried in a vacuum desiccator on calcium chloride. The yield was 65% (1.0 g) and showed a decomposition temperature of 225°C. The percent nitrogen for $C_{16}H_{20}N_2O_2$, Calcd: 10.29%, Found: 10.44%. The molecular weight for, $C_{16}H_{20}N_2O_2$, Calcd: 272.0 g mol⁻¹, Found 272.4 g mol⁻¹. IR and UV spectra of Schiff base were recorded to obtain information about the structure of the Schiff base. The complexation of cobalt (II) ions with N,N' -bis(acetylacetonato)-*o*-phenylenediamine Schiff base was carried out by reacting 5.0 mmol (1.36 g) of Schiff base with 5.0 mmol (1.1896 g) of cobalt chloride in DMF under reflux at 60–70°C for 8 hrs. The solution on cooling has produced a brown colored precipitate of cobalt (II) complex (Yield: 68%, m.p 280°C). The IR and UV spectra of the cobalt (II) complex were recorded for structural information and coordination sited of the ligand with the cobalt (II) ions.

Synthesis of Functionalized Crosslinked Polymer Beads

To prepare a immobilized cobalt (II) complex, the crosslinked polymer beads were prepared by suspension copolymerization of styrene and allylchloride in the presence of divinylbenzene as a crosslinking agent. A 40.0 ml solution of styrene (48.97 mmol, 5.1 g), divinylbenzene (1.50 mmol, 0.195 g) and allylchloride (48.97 mmol, 3.746 g) in DMF was added dropwise in a three-necked round bottom flask containing 500 ml deaerated solution of gelatin (0.75 g), bentonite (2.0 g), boric acid (2.5 g) and polyvinylalcohol (1.5 g) in water. To initiate copolymerization, 10.0 ml deaerated solution of azobisisobutyronitrile (9.0×10^{-4} mmol, 0.15 g) in DMF was added dropwise in a three necked round bottom flask under vigorous stirring and heating at 70°C. After 6 hrs, the heating was stopped and stirring was continued for another 30 min to dissipate the heat of copolymerization. The polymer beads so obtained were separated and washed with methanol (4 × 50 ml) to



Scheme 1.

remove unreacted monomers and initiator. Finally, beads were washed with distilled water to remove bentonite and dried in vacuum oven at 70°C for 24 hrs which produced 6.33 g yellow colored beads (Yield: 70%, m.p. 450°C). The IR spectrum of the dried beads was recorded on KBr pallets that exhibited absorption bands at 1260 cm^{-1} for C—Cl group in the polymer beads.^[50] The amount of allylchloride was found to be 4.90 mmol g^{-1} of beads (Type III) estimated with content of chlorine in the beads (Cl, 17.04%). The beads of other crosslinked densities were prepared by varying the amount of DVB from 0.8 mmol to 2.0 mmol in the reaction mixture, which produced beads with a different amount of allylchloride ranging from 5.80 mmol to 4.46 mmol g^{-1} of beads (Table 1a).

Synthesis of Polymer Anchored N,N'-bis(Acetylacetonate)o-phenylenediamine Schiff Base

The polymer beads of variable crosslinked density were used to anchor N,N'-bis(acetylacetonate)o-phenylenediamine Schiff base synthesized separately. To increase the extent of Schiff base anchoring, the beads (Type III) were swollen for 24 hrs in dimethylformamide (DMF) before anchoring the Schiff base. The swollen beads (1.0 g) were added in a 20 ml solution of dimethylformamide (DMF) containing 2.5 mmol (0.68 g) of N, N'-bis(acetylacetonate)o-phenylenediamine Schiff and refluxed for 8 hrs at 60–70°C under stirring. After cooling, the beads were washed with DMF and methanol and dried in vacuum oven at 60°C (Yield: 70%, 1.176 g). The amount of Schiff base anchored on beads was estimated with a nitrogen percent. The extent and nature of Schiff base anchored on polymer beads have shown dependence on the degree of crosslinking (Table 1a). The beads prepared (Type I–II) with a low amount of divinyl benzene

Table 1a. Composition and characteristics of synthesized crosslinked beads.

Types of beads	DVB in reaction mixture (mmol)	Amount of allylchloride mmol g ⁻¹ beads	% Cl in beads	Beads size (μm)	ρ (g cm ⁻³)	S (%)
I	0.80	5.80	20.59	214.0 ± 0.02	0.39	8.65
II	1.15	5.10	18.18	208.0 ± 0.01	0.42	6.23
III	1.50	4.90	17.40	205.0 ± 0.01	0.46	4.83
IV	1.75	4.80	17.04	201.0 ± 0.03	0.48	4.02
V	2.00	4.46	15.83	196.0 ± 0.02	0.51	3.90

[Styrene]_I = 48.97 mmol, [Allylchloride]_I = 48.97 mmol, DVB (Divinylbenzene), S (Swelling). SD of mean of five measurements.

(<1.50 mmol) have shown a Schiff base on a single polymer chain (Structure-II in Scheme-1) and beads (Type-III–V) obtained at high concentration of divinylbenzene (≥1.50 mmol), were having Schiff base between two polymeric chains (Struct. III in Sch. 1). The 1.0 g beads of Type III were having 1.96 mmol of Schiff base (Table 3). The IR spectrum of polymer anchored Schiff base was recorded and used as evidence for a Schiff base anchoring on polymer support.

Loading of Cobalt (II) Ions on Polymer Anchored N,N'-bis(Acetylacetonate)-o-phenylenediamine Schiff Base

To metallate the polymer anchored N,N'-bis(acetylacetonate)-o-phenylenediamine, the beads were allowed to swell for 24 hrs in dimethylformamide before reacting with the salt of cobalt (II) ions. To load cobalt (II) ions, 1.0 g swollen beads were added in 30 ml dimethylformamide (DMF) containing CoCl₂ · 6H₂O (5.0 mmol, 1.1896 g) and refluxed to 95°C for 8 hrs under stirring conditions. On cooling, the beads were separated and washed with water to remove uncomplexed salt and impurities. On drying in vacuum at 80°C, the brown coloured beads were obtained (Yield: 68%, 1.488 g). The extent of cobalt (II) ions loading has shown dependence on type of beads as clear from the data shown in Table 1b. The loading of cobalt (II) ions on beads with low (<1.50 mmol) and high (≥1.50 mmol) concentration of divinylbenzene has been shown in Sch. 2 as Struct. IV (Beads Type I and II) and Struct. V (Beads-Type III–V), respectively. The IR spectra of Co (II) ions loaded beads were used to confirm the Schiff base bonding with cobalt (II) ions (Table 2a). The UV spectra of cobalt (II) ions loaded beads were also recorded and used as evidence for coordination of cobalt (II) ions with a polymer anchored Schiff base (Table 2b).

To evaluate the loading of cobalt (II) ions, 1.0 g cobalt (II) ions loaded beads were placed in a conical flask containing 20 ml 4 N acetic acid and refluxed for 2 hrs at 110°C. On cooling, the beads were separated and washing was collected carefully to estimate the leached amount of cobalt (II) ions with atomic absorption spectrophotometer at λ_{max} = 240.7 nm. The extent of cobalt (II) ions loading has been evaluated with respect to an available amount of ligand on polymer support and cobalt (II) ions taken initially for

Table 1b. Characteristics of Schiff base anchored crosslinked beads.

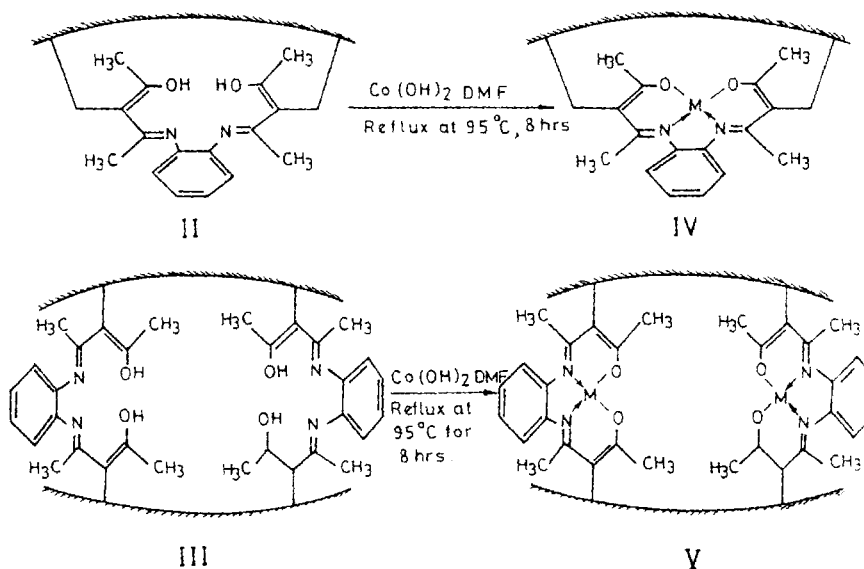
Types of beads	% of allylchloride consumed on anchoring of Schiff base	% of Nitrogen in Schiff base anchored beads	Weight of Schiff base anchored mmol g^{-1} beads	Weight of Co(II) ions loaded mmol g^{-1} beads	EL (%)	EC (%)
I	52.41	4.36	1.52	0.82	16.41	54
II	71.37	5.23	1.84	1.21	24.29	66
III	80.00	5.32	1.96	1.37	27.44	70
IV	70.83	4.88	1.70	0.95	19.04	56
V	65.47	4.20	1.46	0.70	14.01	48

$[\text{Schiff base}]_1 = 5.0 \text{ mmol}$, $[\text{Co(II)}]_1 = 5.0 \text{ mmol}$.

loading and has been presented as efficiency of complexation (% EC) and efficiency of loading (% EL), respectively using the following equations:

$$\% \text{ EC} = \frac{\text{Amount of Co(II) ions loaded } \text{g}^{-1} \text{ of beads}}{\text{Amount of ligand available for complexation } \text{g}^{-1} \text{ of beads}} \times 100$$

$$\% \text{ EL} = \frac{\text{Amount of Co(II) ions loaded } \text{g}^{-1} \text{ of beads}}{\text{Amount of Co(II) ions taken for complexation}} \times 100$$

**Scheme 2.**

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Table 2a. IR frequencies of N,N'-bis(acetylacetonato)-o-phenylenediamine Schiff base ligand and its Co(II) complex.

Metal ion	Functional groups	Frequencies of unsupported		Frequencies of polymer supported	
		Ligand (cm ⁻¹)	Complex (cm ⁻¹)	Ligand (cm ⁻¹)	Complex (cm ⁻¹)
Co(II)	$\nu(\text{OH})$	2936–3323	—	2932–3317	—
	$\nu(\text{C}=\text{O})$ (enolic)	1108–1158	1066	1113–1167	1030
	$\nu(\text{C}=\text{N})$	1626	1620	1623	1586
	$\nu(\text{C}=\text{C})$	1576	1570	1572	1520
	$\nu(\text{M}=\text{O})$	—	533	—	526
	$\nu(\text{M}=\text{N})$	—	428	—	423
	$\nu(\text{C}=\text{Cl})$	—	—	1260	1263

The loading capacity of the beads for cobalt (II) ions has shown dependence on the degree of crosslinking and amount of the N,N'-bis(acetylacetonato)-o-phenylenediamine Schiff base anchored on beads. The 1.0 g beads (Type III) obtained with an optimum amount of divinylbenzene were having 1.37 mmol of cobalt (II) ions (Table 1b).

Evaluation of Catalytic Activity of Polymer Anchored N,N'-bis(acetylacetonato)-o-phenylenediamine Cobalt (II) Schiff Base Complex

To evaluate the effect of heterogenization of cobalt (II) complex, the rate of decomposition of hydrogen peroxide has been evaluated in the presence of polymer bound and unbound cobalt (II) complex under similar experimental conditions. The decomposition rate of hydrogen peroxide was estimated by adding 100 mg cobalt (II) ions loaded beads in

Table 2b. Electronic and magnetic properties of N,N'-bis(acetylacetonato)-o-phenylene diamine Schiff base and its Co(II) complex.

Metal ion	Electronic transitions	Frequencies of transitions of unsupported		Frequencies of transitions of supported		μ_{eff} (BM)	Structure
		Ligand (λ_{max} /nm)	Complex (λ_{max} /nm)	Ligand (λ_{max} /nm)	Complex (λ_{max} /nm)		
Co (II)	$\Pi \rightarrow \Pi^a$	270	255	268	253	1.82 (1.80) ^a at 294K	Square
	$n \rightarrow \Pi^a$	306	263	303	260		Planar
	$\text{C} \rightarrow \text{T}$	—	284	—	282		
	$d \rightarrow d$	—	—	—	—		

^a μ_{eff} of supported complex.

100 ml solution of hydrogen peroxide of known molarity prepared with 2.0 volume (0.6% W/W) stock solution of hydrogen peroxide. The reaction mixture was thermostated to $25.0 \pm 0.1^\circ\text{C}$ under constant stirring. The extent of decomposition of hydrogen peroxide was determined by taking 5.0 ml aliquot of the reaction mixture at different intervals of time and titrated with 0.01 M KMnO_4 solution in the presence of 0.01 M sulfuric acid. A similar procedure was repeated to estimate the extent of decomposition of hydrogen peroxide in the presence of unbound cobalt (II) complex. In order to evaluate other kinetic parameters, the reaction rate was also studied at different concentrations of hydrogen peroxide and different temperatures. To study the effect of concentration of polymer bound cobalt (II) ions on decomposition of hydrogen peroxide, beads of the same cobalt (II) ions loading capacity were used to avoid a structural effect of beads on decomposition of hydrogen peroxide.

RESULTS AND DISCUSSION

The attachment of the reactive species to polymer support results in new reactivity and selectivity. However, the variation in these properties of the species depends upon the type of support, structure of bridging group between reactive species and support and essentially the number and distribution of species on polymer support predominate on other factors which contributed toward property variation of species on immobilization. The crosslinked chloromethylated polystyrene and inorganic non-flexible supports have been used frequently for binding the reactive species, but they require replacement with more flexible support to twist to the size of the anchoring ligand and keep reactive species away from the support. The synthesized crosslinked copolymer beads of styrene and allylchloride have been found to be a more effective substitute to routinely used crosslinked chloromethylated polystyrene support due to its high flexibility in the binding of Co (II) ions by anchored ligand and its significant stability. The prepared copolymer is flexible, stable and anchors ligand effectively for binding cobalt (II) ions. The crosslinked polyallylchloride-styrene matrix is more compatible with dimethylformamide in comparison to crosslinked polystyrene. The compatibility of the polymer matrix in polar solvents affects the extent of reaction. The synthesized matrix has been found to be useful support due to its compatibility in organic solvents. The synthesized beads have shown a variation in the content of allylchloride from 5.80–4.46 mmol g^{-1} of beads on varying the amount of DVB from 0.8 mmol to 2.0 mmol in the reaction mixture (Table 1a). The arrangement of Schiff base on beads has shown a variation due to the variation in the content of allylchloride and the formation of crosslinks between polymeric chains. The beads (Type I and II) obtained at low concentration of divinylbenzene (< 1.5 mmol) have shown arrangement of Schiff base as shown in Struct. II (Sch. 1) and beads (Type III–V) formed at a high amount of divinylbenzene (≥ 1.5 mmol) had an arrangement of Schiff base as shown in Struct. III (Sch. 1). These structures have been proposed on comparing the variation in the amount of allylchloride on polymer beads and its reaction with the Schiff base. The content of allylchloride and Schiff base have been determined by estimating the content of chlorine and nitrogen before and after anchoring the Schiff base on the beads. The beads (Type III) with optimum concentration of divinylbenzene (1.5 mmol) were having 4.90 mmol of allylchloride and 1.96 mmol of Schiff base g^{-1} of beads (Table 1a,b). The polymer bound acetylacetone has been reported^[51] as 0–0 donor for transition metals, hence, a N_2O_2 group of anchored $\text{N,N}'$ -bis(acetylacetone)-o-phenylenediamine Schiff base has been found to be more

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useful^[52] to bind cobalt (II) ions than acetylacetone alone. The Schiff base of acetylacetone with *o*-phenylenediamine offers optimum hydrophilicity required in reactions occurring in the aqueous phase. The extent of Schiff base on polymer support has shown a significant dependence on the degree of crosslinking (Table 1a,b). The density, pore size, and structure of the polymer matrix have shown variations on varying the concentration of divinylbenzene in the reaction mixture. These variations in the structure and arrangement of monomers in the crosslinked beads have resulted in beads with a different degree of swelling and catalytic activities. The beads size has decreased from 214 μm to 196 μm on increasing the divinylbenzene concentration from 0.80 mmol to 2.0 mmol (Table 1a). The beads with 1.50 mmol of divinylbenzene (Type III in Sch. 1) had the highest amount of *N,N'*-bis(acetylacetone) *o*-phenylenediamine Schiff base (1.96 mmol g^{-1} beads) and also showed the highest efficiency for loading (27.44%) and complexation (70%) of cobalt (II) ions (Table 1b). The bead size and degree of swelling in beads were determined by a scanning electron microscope (SEM) as shown in Table 1a. The beads prepared with 1.50 mmol of divinylbenzene (Type III in Sch. 1) have shown a degree of swelling of 4.83% in dimethylformamide as determined with size variation in the beads before (Fig. 1A) and after swelling (Fig. 1B). The thermograms of the unmetallated and metallated polymer anchored Schiff base have indicated a substantial increase in thermal stability as is clear from the TG curves of unmetallated (Fig. 2A) and metallated (Fig. 2B) polymer anchored Schiff base. The increase in thermal stability is an indication for Co (II) ions complexation with a polymer anchored Schiff base which has suggested that a heterogenized cobalt (II) complex could be used as a catalyst for reactions operating at high temperature. The structure and characteristics of homogenized and heterogenized cobalt (II) complexes play a significant role in the catalysis of the reactions, hence, the structure of cobalt (II) complex has been analyzed using IR and UV spectra.

Synthesis and Characterization of Homogeneous Cobalt (II) Schiff Base Complex

The polymer unbound *N,N'*-bis(acetylacetone)*o*-phenylenediamine cobalt (II) Schiff base complex was synthesized (Struct. I in Sch. 1) by reacting equimolar amounts of *N,N'*-bis(acetylacetone)*o*-phenylenediamine and cobalt (II) chloride in dimethylformamide under reflux at 95°C for 8 h. The comparison of IR spectra of pure Schiff base and its cobalt (II) complex has provided ample evidences for the coordination of cobalt (II) ions through enolic oxygen and azomethine nitrogen of the Schiff base. The vibrational frequency of azomethine $\nu(\text{C}=\text{N})$ of free Schiff base on coordination with cobalt (II) ions is shifted from 1626 cm^{-1} to 1620 cm^{-1} and frequency corresponding to $\text{C}=\text{C}$ bond has also shown a shift from 1576 cm^{-1} to 1570 cm^{-1} (Table 2a). The absorption band between 1108–1158 $\nu(\text{C}-\text{O})$ of free ligand has shifted to 1066 cm^{-1} due to the coordination of cobalt (II) ions with enolic oxygen. The original absorption band of enolic $-\text{OH}$ of free Schiff base observed between 2936–3323 cm^{-1} was missing completely in the spectrum of cobalt (II) complex which was a clear indication of coordination of cobalt (II) ions with enolic oxygen (Table 2a). The appearance of two new bands in cobalt (II) complex at 533 cm^{-1} and 428 cm^{-1} is due to the coordination of cobalt (II) ions with enolic oxygen ($\text{M}-\text{O}$) and azomethine nitrogen ($\text{M}-\text{N}$) of the Schiff base. These IR absorption data

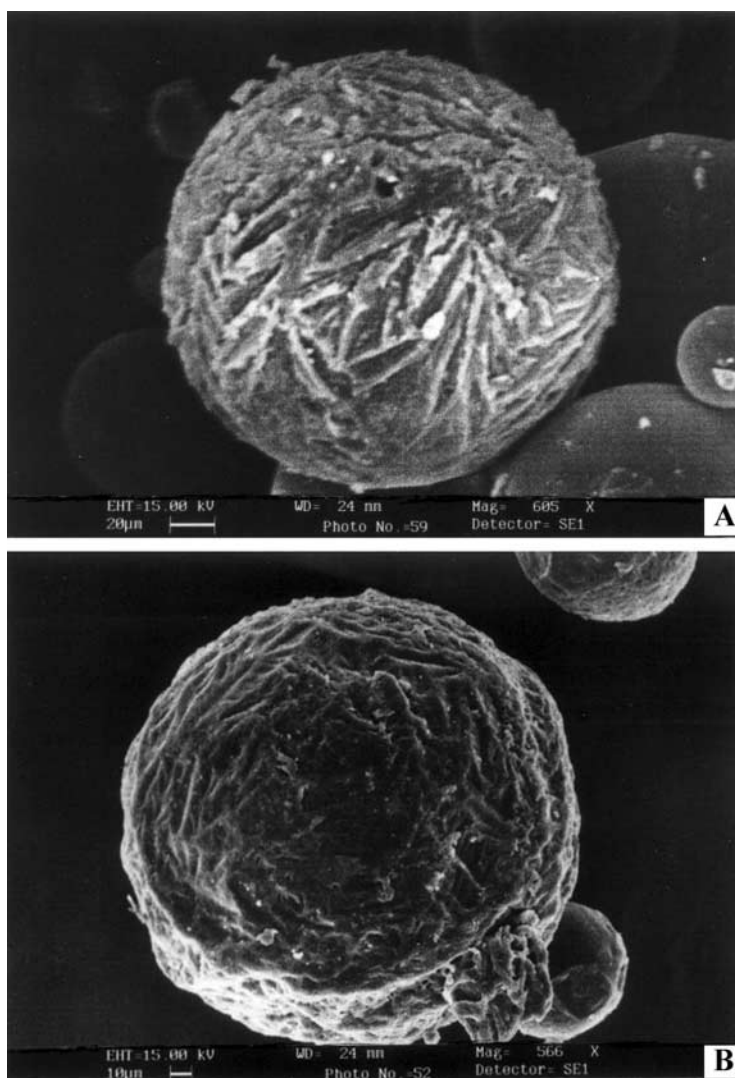


Figure 1. Scanning electron micrographs of crosslinked polymer beads before (A) and after swelling (B).

were suggestive of tetradentate coordination of cobalt (II) ions with the Schiff base and for square planar geometry of the complex. The electronic spectra of the Schiff base has also shown a shift in transition frequencies corresponding to $\Pi \rightarrow \Pi^*$ and $n \rightarrow \Pi^*$ transitions (Table 2b). The absorption band at 270 nm ($\Pi \rightarrow \Pi^*$) has been shifted to 255 nm ($\Pi \rightarrow \Pi^*$) on coordination with cobalt (II) ions. The appearance of a new absorption band at 284 nm on coordination of Schiff base with cobalt (II) ions is an indicative of charge transfer process (CT) between ligand to metal (L \rightarrow M). The cobalt (II) complex is paramagnetic with a magnetic moment (μ) of 1.80 BM at 294K corresponding to one

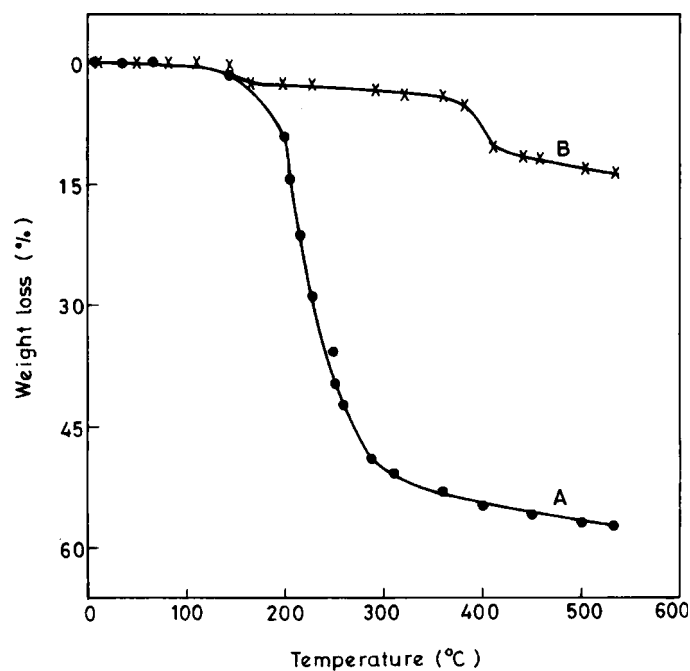


Figure 2. TG curves for polymer anchored Schiff base (A) and its cobalt (II) complex (B).

unpaired electron in the complex, hence, it has indicated for square planar geometry of the complex analogue to other quadridentate chromophore (N_2O_2).^[52,53]

Synthesis and Characterization of Polymer Bound Cobalt (II) Schiff Base Complex

The heterogenization of the complex on the polymer support results in increased catalytic activity provided the polymer anchored ligand is able to form a complex of the same geometry as found with the free ligand. To obtain a similar structure of the complex, the number and distribution of ligand anchoring sites on the polymer support plays an important role, hence, the matrix design using suitable composition of the monomers and crosslinkers in the reaction mixture is an important step. The structural information and catalytic activity of the heterogenized complex have provided sufficient opportunities to optimize the composition of the matrix to obtain a cobalt (II) complex with similar geometry as found with an unsupported cobalt (II) complex. To synthesize the heterogenized N,N' -bis(acetylacetonato)-phenylene diamine cobalt (II) complex, the crosslinked polymer beads were first reacted with Schiff base under reflux at 60–70°C for 8 h (Struct. II and III in Sch. 1) and subsequently, loaded with cobalt (II) ions (Struct. IV and V in Sch. 2). The amount of a Schiff base anchored on polymer beads has shown a dependence on the amount of allylchloride in crosslinked beads whereas, the amount and



arrangement of allylchloride in polymer chains have shown dependence on a relative amount of divinylbenzene and allylchloride placed initially in the reaction mixture. The beads (Type I and II) prepared with low amount of the divinylbenzene (< 1.5 mmol) in the reaction mixture were having sufficient amount of allylchloride in the polymer chains but attachment of Schiff base in these beads (Type I and II) was poor (1.52 – 1.84 mmol g^{-1} of beads) because in these type of beads, the ligand was attached to the backbone of a single polymer chain (Struct. II in Sch. 1). The polymer beads (Type III) obtained at high concentration of divinylbenzene (1.5 mmol) were having low amount of allylchloride (4.90 mmol g^{-1} of beads) but shown improved efficiency for anchoring of Schiff base (80%) on polymer support (Struct. III in Sch. 1). On further increasing the amount of divinylbenzene (> 1.5 mmol), the amount of allylchloride and its consumption in anchoring of Schiff base was decreased (< 1.96 mmol g^{-1} of beads) as clear from the data shown in Table 1a,b. The amount of allylchloride and Schiff base on polymer support has been evaluated by estimating the content of chlorine and nitrogen in the matrix. The beads prepared with different amount of divinylbenzene have shown variation in Schiff base content from 1.52 – 1.46 mmol g^{-1} of beads and allylchloride from 5.80 – 4.46 mmol g^{-1} of beads (Table 1a,b). The beads prepared with a high amount of divinylbenzene (> 1.5 mmol) have shown a decreasing trend in the amount of anchored Schiff base due to the decrease in porosity (< 0.62 cm^3 g^{-1}) on increasing the degree of crosslinking. The amount of cobalt (II) ions on beads of different crosslinked densities has been evaluated in terms of initial amount of cobalt (II) ions (%EL) and the amount of Schiff base available for complexation at the beads (%EC). These two parameters have shown a variation in the degree of crosslinking and the arrangement of the Schiff base on the polymer support. The data shown in Table 1b have clearly indicated that the efficiency of loading (%EL) and complexation (%EC) of Co (II) ions have increased up to 1.50 mmol of the divinylbenzene (Type III) and on further increasing the amount of divinylbenzene beyond 1.50 mmol both the efficiency of loading (%EL) and complexation (%EC) have decreased (Table 1b). The extent of complexation of cobalt (II) ions on beads has been supported with IR spectra recorded on KBr pallets. The IR spectrum of polymer anchored Schiff base has shown absorption bands at 1572 cm^{-1} $\nu(\text{C}=\text{C})$, 1623 cm^{-1} $\nu(\text{C}=\text{N})$ and a broad band between 2932 cm^{-1} to 3317 cm^{-1} due to $\nu(\text{OH})$, which have strongly supported the anchoring of Schiff base on polymer beads. The absorption band between 1113 – 1167 cm^{-1} was attributed to vibrational frequency corresponding to $\nu(\text{C}-\text{O})$ enolic band in the Schiff base has shifted to 1526 cm^{-1} after complexation. The electronic spectra of Schiff base anchored polymer beads have shown bands at 268 nm and 303 nm corresponding to $\Pi \rightarrow \Pi^*$ and $n \rightarrow \Pi^*$ electronic transitions (Table 2b). Thus, the appearance of characteristic bands in IR and UV spectra of polymer anchored Schiff base has provided sufficient evidence for the anchoring of a Schiff base on the polymer support. The complexation of cobalt (II) ions on polymer anchored Schiff base has been verified with IR and UV spectra of polymer anchored Schiff base and its cobalt (II) complex. The IR absorption band corresponding to $\nu(\text{C}=\text{C})$ group has been shifted from 1572 cm^{-1} to 1520 cm^{-1} and the band due to $\nu(\text{C}=\text{N})$ has shifted from 1623 cm^{-1} to 1586 cm^{-1} . The broad band between 2932 – 3317 cm^{-1} due to $\nu(\text{OH})$ in polymer anchored Schiff base has disappeared on complexation with cobalt (II) ions. The appearance of two new bands at 526 cm^{-1} and 423 cm^{-1} for $\text{M}-\text{O}$ and $\text{M}-\text{N}$ bonds has further supported the complexation of the cobalt (II) ions on the polymer anchored Schiff base. The electronic



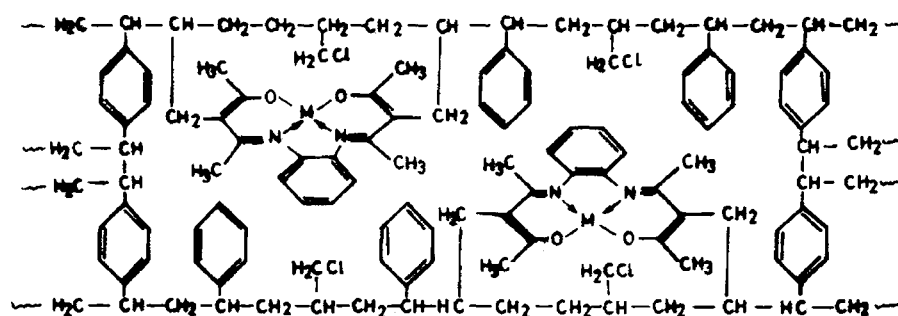
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spectra of the polymer anchored Schiff base on complexation with cobalt (II) ions have shown variations in absorption bands corresponding to $\Pi \rightarrow \Pi^*$ and $n \rightarrow \Pi^*$ transitions observed in polymer anchored Schiff base. The bands corresponding to $\Pi \rightarrow \Pi^*$ and $n \rightarrow \Pi^*$ transitions have been changed from 268 nm to 253 nm and from 303 nm to 260 nm on complexation of cobalt (II) ions with a polymer anchored Schiff base (Table-2b). The appearance of a new absorption band at 282 nm is attributed to a charge transfer (CT) from ligand to metal ions ($L \rightarrow M$). These variations in IR and UV frequencies have provided evidence for the complexation of the cobalt (II) ions on the polymer anchored Schiff base. The IR and UV absorption bands of homogenized and heterogenized cobalt (II) complex have shown a very small variation in their position, which has clearly indicated that the polymer has provided sufficient flexibility to the ligand to create an environment analogous to the free complex. The magnetic moment (μ) of the polymer supported cobalt (II) complex has been found to be 1.82 BM at 294K, which corresponds to one unpaired electron in the cobalt (II) ions in the complex. It has provided evidence for square planar geometry of the complex on polymer support. The spectral and magnetic data have clearly indicated that *N,N'*-bis(acetylacetonato)-phenylenediamine cobalt (II) complex on polymer support has a similar structure as in the free state. The structure of the complex has not shown any variation within the studied concentration range of divinylbenzene.

Degree of Swelling and Complexation Behavior of Polymer Beads

The extent of complexation and catalytic behavior of metal ions on polymer matrix depend upon the degree of swelling of matrix in the solvent used for complexation and as a reaction media. The degree of swelling of the network structure in the solvent ultimately depends upon the lyophilic nature of the matrix and the degree of crosslinking between polymeric chains. On swelling, the polymer anchored Schiff base has become accessible to Co(II) ions for complexation and also increased the solvent mediated diffusion of the reacting molecules to the active sites on the polymer backbone. It has also improved the diffusion of the product from the active sites to the surface of the network structure. The swelling adds flexibility in polymer anchored ligand to provide suitable orientations of the active sites to interact with reacting molecules. The swelling of prepared beads in different solvents has been studied but dimethylformamide (DMF) has shown significant swelling. The acetylacetonato and phenyl groups of the ligand have struck a balance for swelling due to their lyophilic and lyophobic behavior toward dimethylformamide. The prepared beads (Type I–V) have shown significant variations in degree of swelling (%S) in dimethylformamide as shown in Table 1a. The beads prepared with a low amount of divinylbenzene (0.8 mmol) have shown the highest degree of swelling (8.65%) in comparison to beads with a high amount of divinylbenzene (2.0 mmol). The beads (Type I) with a high degree of swelling (8.65%) were having a low amount of polymer anchored Schiff base (1.52 mmol g^{-1} of beads) and Co(II) ions (0.82 mmol g^{-1} of beads). These beads were having cyclic arrangement of Schiff base (Table-1b) on polymeric backbone (Struct. II in Sch. 1). The high amount of allylchloride (5.80 mmol g^{-1} of beads) has facilitated the attachment of a Schiff base on the same polymeric chains (Network structure VIA and Struct. II in Sch. 1).

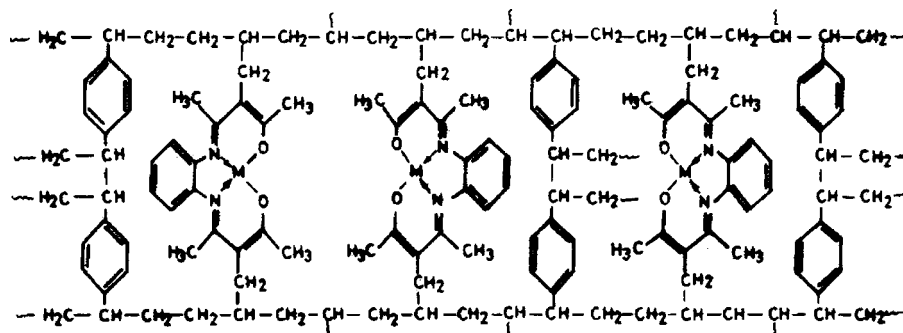


Network structure VIA. Network structure of beads at low concentration of DVB (VI-A).

This Schiff base pattern on the polymeric backbone has left other sites stereospecifically inaccessible for Schiff base, hence, the amount of Schiff base was low (1.52 mmol g^{-1} of beads). This pattern of the Schiff base on the single polymer backbone has also decreased the extent of complexation of cobalt (II) ions on the available Schiff base, hence, beads (Type I and II) with network structure VIA have shown low efficiency for complexation (%EC) and loading (%EL) for Co (II) ions as shown in Table 1b. This network structure (VIA) was having high porosity ($>0.62 \text{ cm}^3 \text{ g}^{-1}$) due to a low degree of crosslinking between polymeric chains (Beads Type I and II). These beads (Type I and II) were having a high degree of swelling, but have shown low catalytic activity. The beads prepared with 1.5 mmol of divinylbenzene in the reaction mixture (Type III), the amount of allylchloride (4.90 mmol g^{-1} of beads) and Schiff base (1.96 mmol g^{-1} of bead) was optimum but showed a decreasing trend on increasing divinylbenzene beyond 1.50 mmol in the reaction mixture (Table 1a and b). At a high amount of divinylbenzene in the reaction mixture ($\geq 1.5 \text{ mmol}$), the network structure (Network structure VIB) was different which has facilitated the attachment of Schiff base between two polymeric chains (Struct. III in Sch. 1). This arrangement of Schiff base has increased the efficiency of complexation (%EC) and loading (%EL) of cobalt (II) ions. This network structure (Network structure VIB) has shown a high degree of crosslinking and low porosity ($<0.62 \text{ cm}^3 \text{ g}^{-1}$). In this network structure (Network structure VIB), the degree of swelling was also low in comparison to the network structure obtained at a low amount of divinyl benzene (Network structure VIA). The beads (Type III) produced with 1.5 mmol of divinylbenzene have shown a optimum degree of swelling (4.83%) with the highest efficiency for complexation (%EC) and loading (%EL) of cobalt (II) ions, hence, showed the highest catalytic activity (Table 1a,b). At a high concentration of the divinylbenzene ($>1.50 \text{ mmol}$), the increased degree in crosslinking has reduced the efficiency of complexation (%EC) and loading (%EL) for cobalt (II) ions due to a substantial decrease in the amount of polymer anchored Schiff base and its complexation with cobalt (II) ions due to the decrease in porosity ($<0.62 \text{ cm}^3 \text{ g}^{-1}$) and degree of swelling ($<4.83\%$) which has prevented the complexation of cobalt (II) ions at polymer anchored Schiff base. The beads (Type III–V) obtained at a high amount of divinylbenzene ($\geq 1.5 \text{ mmol}$) were compact with a decreasing trend in their size from $214 \mu\text{m}$ to $196 \mu\text{m}$ and an increasing trend in their density from 0.39 g cm^3 to 0.51 g cm^{-3} . These investigations have clearly

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Network structure VIB. Network structure of beads at a high concentration of DVB (VI-B).

indicated that beads (Type III) prepared at 1.5 mmol of divinylbenzene were having optimum composition to show the highest catalytic activity, hence were used for evaluation of kinetic parameters for decomposition of hydrogen peroxide under different experimental conditions.

Evaluation of Catalytic Activity of Polymer Supported *N,N'*-bis(Acetylacetonate)-*o*-phenylenediamine Cobalt (II) Schiff Base Complex

The catalytic activity of polymer supported *N,N'*-bis(acetylacetonate)-*o*-phenylenediamine cobalt (II) complex has been evaluated by comparing the rate of decomposition of hydrogen peroxide in the presence of free and polymer supported cobalt (II) complex. The activity of the catalyst has been evaluated at different concentrations of the hydrogen peroxide and supported catalyst. The catalytic activity of supported catalyst was also studied at different temperatures to determine the effect of support and energy of activation for decomposition of the hydrogen peroxide. The amount of supported catalyst in the reaction mixture was varied by taking different weight of the same loading capacity, so that the structural effect of the beads is minimized. The cobalt (II) complex loaded beads were kept in dimethylformamide for swelling before using them in the reaction mixture. The rate of decomposition of hydrogen peroxide has been studied using beads of optimized loading capacity (Type III) at constant pH (8.0) and ionic strength (0.1 mol dm^{-3}) of the medium. The decomposition of hydrogen peroxide at different intervals of time was evaluated as shown in Fig. 3. The logarithmic value of the remaining concentration of hydrogen peroxide ($a-x$) as a function of reaction time has shown a linear decreasing trend (Fig. 3A) at $1.37 \times 10^{-3} \text{ mol dm}^{-3}$ concentration of the supported catalyst. The decomposition of hydrogen peroxide was also determined using unbound catalyst ($2.5 \times 10^{-3} \text{ mol dm}^{-3}$) at the same concentration of the hydrogen peroxide ($3.57 \times 10^2 \text{ mol dm}^{-3}$), which has also shown a linear decreasing trend (Fig. 3B), but the rate of decomposition was substantially lower ($k = 7.78 \times 10^{-5} \text{ min}^{-1}$) in the homogenized catalyst in comparison to the heterogenized catalyst ($k = 7.03 \times 10^{-3} \text{ min}^{-1}$). However, the trends of decomposition of hydrogen peroxide both in

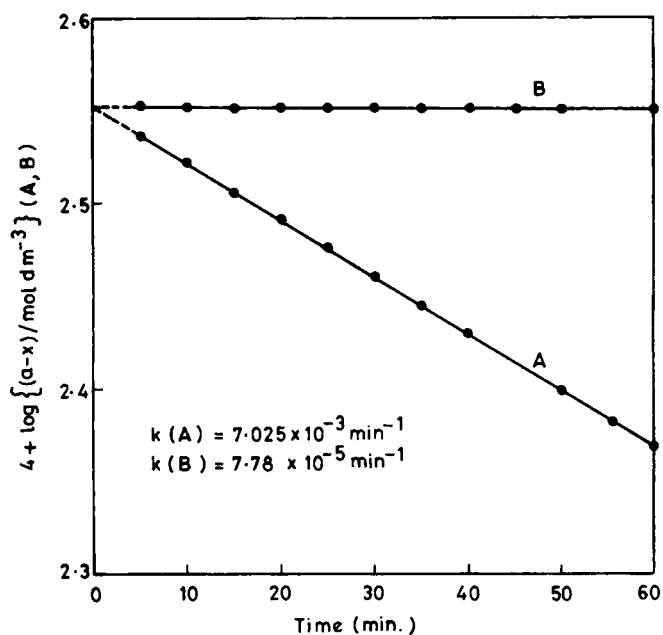


Figure 3. Effect of reaction time on decomposition of H_2O_2 with supported (A) and unsupported; (B) cobalt (II) Schiff base complex. $[\text{H}_2\text{O}_2] = 3.57 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Co (II)}](\text{A}) 1.37 \times 10^{-3} \text{ mol dm}^{-3}$; (B) $2.5 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{pH} = 8.0$, $\mu = 0.1 \text{ mol dm}^{-3}$, $\text{Temp.} = 25^\circ\text{C}$.

the heterogenized and homogenized catalysis were the same, which suggested the existence of a similar mechanism in both cases. The turnover number in the case of heterogenized cobalt (II) ions has been found to be high ($19.02 \times 10^{20} \text{ molecules mol}^{-1} \text{ s}^{-1}$) in comparison to the homogenized cobalt (II) ions ($11.42 \times 10^{18} \text{ molecules mol}^{-1} \text{ s}^{-1}$). The rate of decomposition has also been studied at different concentrations of hydrogen peroxide ranging from $1.79 \times 10^{-2} \text{ mol dm}^{-3}$ to $5.95 \times 10^{-2} \text{ mol dm}^{-3}$ at a constant concentration of heterogenized ($1.37 \times 10^{-3} \text{ mol dm}^{-3}$) and homogenized ($2.5 \times 10^{-3} \text{ mol dm}^{-3}$) cobalt (II) ions. The logarithmic plots between the rate of decomposition (R_p) vs. concentration of hydrogen peroxide (Fig. 4a,b) have shown a linear increasing trend with a slope value of unity both in homogenized (Fig. 4b) and heterogenized (Fig. 4a) cobalt (II) ions. The slope values have clearly indicated that the rate of decomposition of hydrogen peroxide was first order and the hydrogen peroxide has decomposed by a similar mechanism in homogenized and heterogenized conditions. However, the rate of decomposition of hydrogen peroxide was higher in the case of heterogenized Co (II) ions. The high rate of decomposition in the case of heterogenized catalyst was due to the increased efficiency of the catalyst on the polymer support in comparison to the unbound catalyst. The catalytic activity of cobalt (II) ions in decomposition of hydrogen peroxide has also been determined at different concentrations of the catalyst keeping constant the concentration of hydrogen peroxide ($3.57 \times 10^{-2} \text{ mol dm}^{-3}$). The logarithmic plots drawn between the rate of decomposition (R_p) vs. concentration of the cobalt (II) ions have shown a linear increasing trend, both in

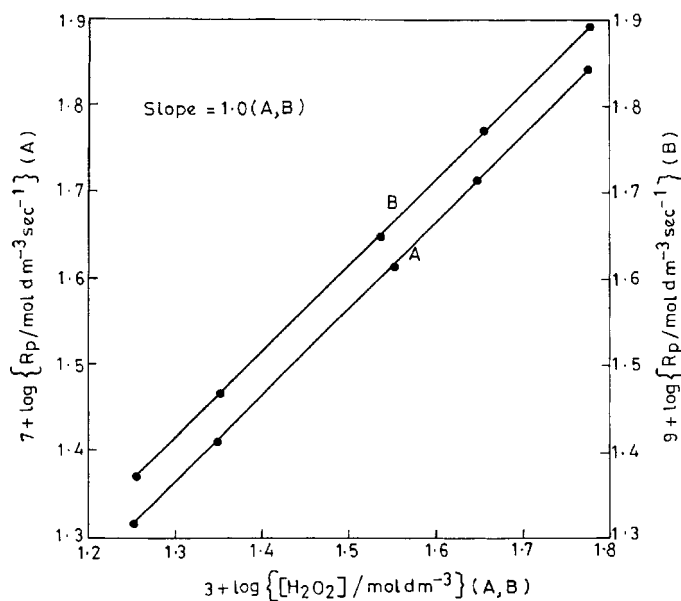


Figure 4. Log-log plot between R_p vs. $[H_2O_2]$ for supported (A) and unsupported (B) cobalt (II) Schiff base complex $[Co(II)]$; (A) $1.37 \times 10^{-3} \text{ mol dm}^{-3}$; (B) $2.5 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{pH} = 8.0$, $\mu = 0.1 \text{ mol dm}^{-3}$, $\text{Temp.} = 25^\circ\text{C}$.

the heterogeneous (Fig. 5a) and homogeneous (Fig. 5b) conditions of cobalt (II) ions. The slope value in both cases was almost the same, which has indicated a first order dependence of reaction rate on concentration rate of cobalt (II) ions. The rate of decomposition of hydrogen peroxide with beads of different loading capacity was also determined and showed an increasing trend in the decomposition of hydrogen peroxide on increasing the loading capacity of the beads. The reaction rate has shown a decreasing trend on increasing the weights of the beads which has been due to the decreasing effect on the turnover number of the beads due to the decrease in intra and interparticles diffusion of reacting molecules on compaction of the beads. These observations have clearly suggested that the efficiency of the catalyst on crosslinked beads would be optimum if reactions are carried out in stirring conditions. The activity of the catalyst was also studied at different temperatures ranging from 20°C to 50°C at a constant concentration of hydrogen peroxide ($3.57 \times 10^{-2} \text{ mol dm}^{-3}$) and catalyst ($1.37 \times 10^{-3} \text{ mol dm}^{-3}$). In order to keep identical conditions, the concentration of unbound catalyst was taken in a similar range ($2.5 \times 10^{-3} \text{ mol dm}^{-3}$) to the concentration of the supported catalyst. The activation energy for decomposition of hydrogen peroxide, both in supported and unsupported conditions was calculated from the Arrhenius plot drawn between $\ln k$ vs. $1/T$ (Fig. 6a,b). The activation energy for the decomposition of hydrogen peroxide in the presence of supported cobalt (II) ions has been found to be low ($42.37 \text{ kJ mol}^{-1}$) in comparison to the homogenized catalyst ($63.59 \text{ kJ mol}^{-1}$) within the same temperature range of 20°C to 50°C . This clearly indicated that polymer support has decreased the energy of activation for decomposition of hydrogen peroxide by providing suitable interactions between

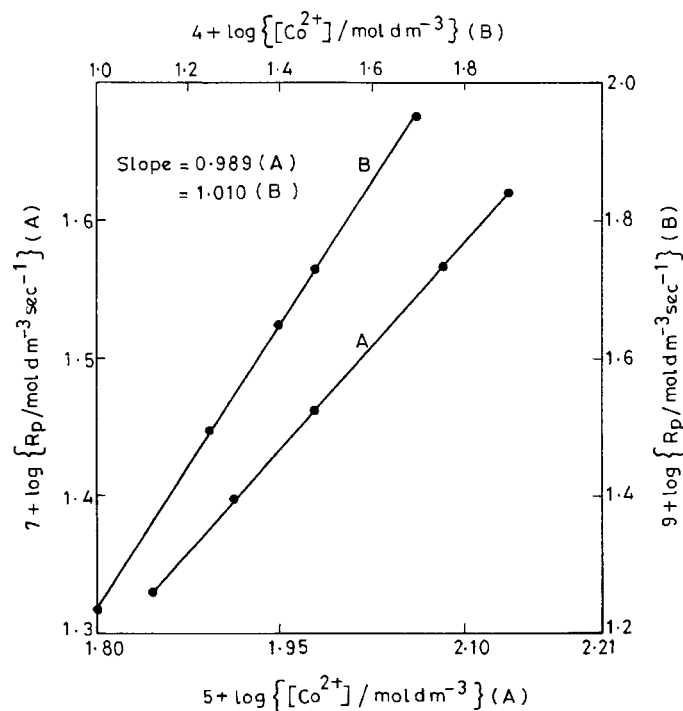


Figure 5. Log-log plot between R_p vs. $[Co(II)]$ with supported (A) and unsupported (B) cobalt (II) Schiff base complex. $[H_2O_2] = 3.57 \times 10^{-2} \text{ mol dm}^{-3}$, $\text{pH} = 8.0$, $\mu = 0.1 \text{ mol dm}^{-3}$, $\text{Temp.} = 25^\circ\text{C}$.

catalyst and hydrogen peroxide in comparison to interactions observed between hydrogen peroxide and the unbound catalyst. This has clearly indicated that polymer support has contributed significantly in providing a suitable microenvironment to the reacting molecules in comparison to the homogeneous catalyst. The rate of decomposition of hydrogen peroxide, both in the presence of supported and unsupported cobalt (II) ions, has been found to decrease on increasing the ionic strength (μ) of the medium from 0.1 mol dm^{-3} to 0.5 mol dm^{-3} . The decreasing trend in the rate of decomposition of hydrogen peroxide on varying the ionic strength of the medium is indicative of involvement of a ionic species during decomposition of the hydrogen peroxide. The variation in hydrogen ions concentration has shown a linear decreasing effect on the rate of decomposition of the hydrogen peroxide (Fig. 7), hence, all experiments were carried out at optimum pH of 8.0. The rate of decomposition of hydrogen peroxide in the presence of heterogenized cobalt (II) ions has been higher in comparison to the unsupported cobalt (II) ions, but the reaction rate has shown a similar dependence on the concentration of hydrogen peroxide, cobalt (II) ions and ionic strength of the medium. The structural data of unbound and polymer bound N,N' -bis(acetylaceton) *o*-phenylenediamine cobalt (II) complex have provided sufficient evidence for a similar structure of $Co(II)$ complex^[54] on

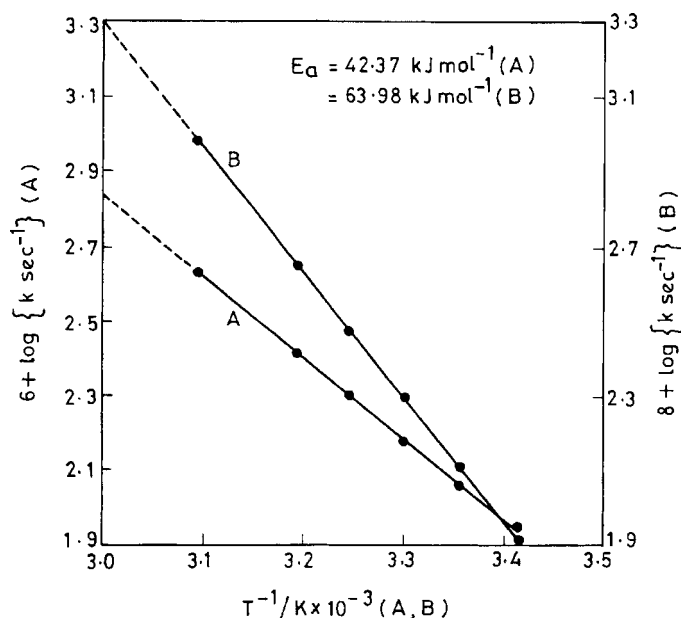
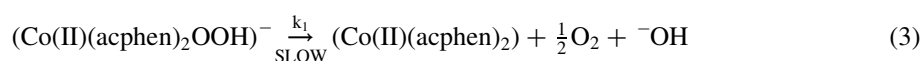
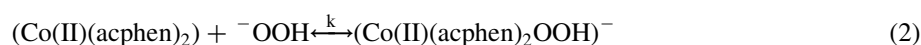


Figure 6. Arrhenius plots for the energy of decomposition of H_2O_2 with supported (A) and unsupported (B) cobalt (II) Schiff base complex. $[\text{H}_2\text{O}_2] = 3.57 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Co (II)}] \text{ (A)} 1.37 \times 10^{-3} \text{ mol dm}^{-3}$, (B) $2.5 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{pH} = 8.0$, $\mu = 0.1 \text{ mol dm}^{-3}$.

the polymer support and in free state, hence, the mechanism for decomposition of hydrogen peroxide in homogenized and heterogenized conditions has also been assumed to be the same and proposed to occur by the following reaction steps:



Considering steps 1–4, the rate expression for the decomposition of hydrogen peroxide is derived as below:

$$\frac{-d[\text{H}_2\text{O}_2]}{dt} = \frac{k_d K k_1 [\text{Co(II)(acphen)}_2] [\text{H}_2\text{O}_2]}{[\text{H}^+]} \quad (5)$$

Where k_d and k_1 are the rate constants for dissociation of hydrogen peroxide and intermediate complex formed by association of HOO^- species. The K is an equilibrium constant for the intermediate complex formed between HOO^- and $(\text{Co(II)(acphen)}_2)$

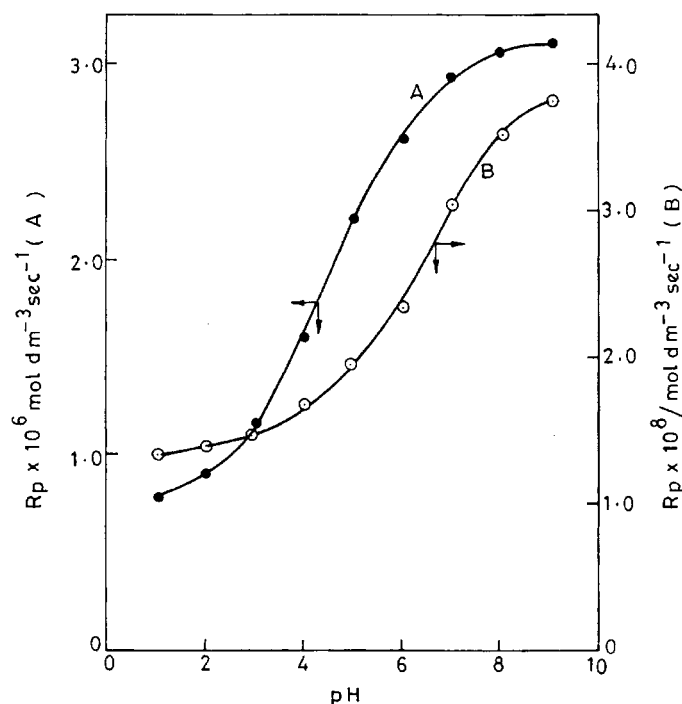


Figure 7. Effect of pH on rate of decomposition (R_p) of H_2O_2 with supported (A) and unsupported (B) cobalt (II) Schiff base complex $[H_2O_2] = 3.57 \times 10^{-2} \text{ mol dm}^{-3}$, $[Co(II)]$ (A) $1.37 \times 10^{-3} \text{ mol dm}^{-3}$, (B) $2.5 \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 0.1 \text{ mol dm}^{-3}$, Temp. = 25°C .

complex. The rate expression (Eq. 5) explains the dependence of the reaction rate (R_p) on the concentration of hydrogen peroxide, cobalt (II) complex and hydrogen ions in the reaction mixture, hence provided support for the proposed steps 1–4 for the decomposition of the hydrogen peroxide using supported and unsupported cobalt (II) Schiff base complex.

CONCLUSION

The heterogenization of N,N' -bis(acetylacetonato)-phenylenediamine cobalt (II) complex on new polymer support has shown a similar structure as observed in homogeneous conditions, but catalytic activity was substantially improved on heterogenization. The extent of immobilization of cobalt (II) ions has been found to be dependent on the degree of crosslinking and composition of the polymer support. The N,N' -bis(acetylacetonato)-phenylenediamine Schiff base has shown a substantial affinity to coordinate with cobalt (II) ions through its N_2O_2 coordinating sites. The reaction rate for decomposition of hydrogen peroxide both in homogeneous and heterogeneous conditions has shown a similar dependence on the concentration of reactants, hence given an



indication for identical mechanism in homogeneous and heterogeneous conditions. The support has increased the efficiency of the catalyst by increasing the catalyst density at the surface in comparison to the homogeneous catalyst.

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