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Synthesis, characterization and catalytic potentials of polymer anchored copper(II), oxovanadium(IV) and dioxomolybdenum(VI) complexes of 2-(α-hydroxymethyl)benzimidazole

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Abstract

2-(α-Hydroxymethyl)benzimidazole (Hhmbmz) has been covalently anchored to chloromethylated polystyrene cross-linked with 5% divinylbenzene. This chelating resin reacts with cupric acetate, vanadyl sulphate and [MoO$_2$(acac)$_2$] (Hacac = acetylacetone) in presence of Hhmbmz to give complexes PS-[Cu(hmbmz)$_2$], PS-[VO(hmbmz)$_2$] and PS-[MoO$_2$(hmbmz)$_2$] (where, PS-hmbmz = deprotonated 2-(α-hydroxymethyl) benzimidazole covalently linked with polymer), respectively. These complexes were characterized by elemental analyses, FT-IR, EPR and electronic spectra, SEM and TGA-DTA methods. EPR results indicate that complexes are well dispersed in the polymeric support. Complexes PS-[Cu(hmbmz)$_2$] and PS-[VO(hmbmz)$_2$] have been used as catalysts for the oxidation of styrene and ethyl benzene while PS-[VO(hmbmz)$_2$] and PS-[MoO$_2$(hmbmz)$_2$] for the oxidative bromination of salicylaldehyde. Oxidation of styrene gives three major products, styrene oxide, benzaldehyde and benzoic acid while ethyl benzene gives acetophenone as the major product. Oxidative bromination of salicylaldehyde using H$_2$O$_2$/KBr gives 5-bromosalicylaldehyde selectively in quantitative yield. EPR spectra of both freshly prepared and recovered catalysts are identical, which indicate that the metal-Schiff base moiety is intact and the coordination environments are not altered during the reaction. © 2005 Elsevier B.V. All rights reserved.

Keywords: Polymer anchored-complexes; Oxidation of styrene and ethyl benzene; Oxidative bromination of salicylaldehyde; 2-(α-hydroxymethyl)benzimidazole

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1. Introduction

Immobilization of homogeneous catalysts onto polymer supports through covalent attachment has received wide attention because these materials offer advantageous features of heterogeneous catalysis to homogeneous systems. The polymer-supported catalysts enhance their thermal stability, selectivity, recyclability and easy separation from reaction products leading to the operational flexibility [1,2]. Chloromethylated polystyrene cross-linked with divinylbenzene is one of the most widely employed macromolecular support for heterogenization of homogeneous catalysts [3–8]. Synthetic organic chemistry and pharmaceutical industry have taken full advantages of such catalysts [9]. The use of polymer-supported catalysis in synthetic organic chemistry have been reviewed recently [10]. In search of new oxidation catalysts, we have isolated and characterized polymer-anchored copper(II), oxovanadium(IV) and dioxomolybdenum(VI) complexes of 2-(α-hydroxymethyl)benzimidazole (**I**) (Scheme 1) and tested their catalytic activities in the oxidation of ethyl benzene and styrene, and oxidative bromination of salicylaldehyde.

Styrene oxide is an intermediate for the manufacture of the perfumery chemical, phenylethyl alcohol and is manufactured industrially by the reaction of benzene and ethylene oxide or by the epoxidation of styrene by NaOCl. Epoxidation of styrene using homogeneous catalysts [11,12] and over titanosilicate zeolites [13,14] or heteropolytungstates [15] have been reported. Recently, [VO(salophen)] [H$_2$salophen = N,N′-bis(salicyledene)phenylene-1,2-diamine] either encapsulated in zeolite-Y or anchored to mesoporous materials Al-MCM-41 has been used as catalyst for the epoxidation of styrene [16].
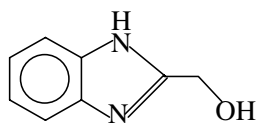
Recently, the development of clean and economically viable processes for the selective oxidation of ethylbenzene to value added product acetophenone [17–22] has attracted research interest. Acetophenone is used as a component of perfumes and as an intermediate in pharmaceuticals, resins, alcohols, esters, aldehydes, and tear gas (chloro acetophenone). It is used as a solvent for cellulose ethers and drug to induce sleep. Currently, acetophenone is produced industrially via the oxidation of ethylbenzene with molecular oxygen using cobalt cycloalkanecarboxylate or cobalt acetate as catalyst in acetic acid solvent [20]. This method suffers from its corrosive nature and environmentally unfriendly. The oxovanadium(IV) complex reported in this paper exhibits remarkable catalytic activity and high selectivity in the catalytic oxidation of ethylbenzene to acetophenone.

Study on the oxidative bromination of organic substrates catalysed by vanadium complexes in presence of halide using H$_2$O$_2$/HClO$_4$ has been considered as model reaction for enzymes vanadate-dependent haloperoxidases (V-HalPO) [23,24]. Though, catalytic oxidation by vanadium complexes is very common [23,25], literature on the oxidative bromination catalyzed by model vanadium complexes is limited [26–29]. Molybdenum analogue has also been reported for catalytic reaction [30,31]. However, no polymer supported vanadium and molybdenum complexes have been reported for such study.

2. Experimental

2.1. Materials

Analytical reagent grade cupric acetate monohydrate, vanadyl sulphate penta hydrate, ammonium heptamolybdate, ethyl benzene and salicylaldehyde were purchased from E. Merck, India. Chloromethylated polystyrene [18.9% Cl (5.3 mmol Cl per gram of resin) and 5% cross-linking with divinylbenzene] was gifted by Thermax Limited, Pune, India. Acetylacetone and styrene were procured from Aldrich Chemical Co. USA. 2-(α-Hydroxymethyl)benzimidazole [32] and [MoO$_2$(acac)$_2$]

Hhmbmz (**I**)

Scheme 1.

(acac = acetylacetonate(−1)) [33] were prepared according to the method reported in the literature.

2.2. Characterization procedures

IR spectra were recorded as KBr pellet on a Perkin–Elmer model 1600 FT-IR spectrometer after grinding the sample with KBr. Diffuse reflectance UV–Vis spectra were recorded on a Shimadzu UV–Vis spectrophotometer (UV-2500 PC) using barium sulfate as the standard. Thermogravimetric analyses of the complexes were carried out using TG Stanton Redcroft STA 780. EPR spectra were recorded on a Bruker EMX X-band spectrometer operating at 100 kHz field modulation at room temperature. The microwave frequency was calibrated using a frequency counter of the Microwave Bridge ER 041 XG-D. Bruker Simfonia and WIN-EPR software packages were used in the spectral simulations and to calculate hyperfine coupling constant. The spectra were recorded at room temperature by taking the crushed powder samples in a suprasil quartz tube. Scanning electron micrographs (SEM) of catalysts were recorded on a Leo instrument model 435 VP. The samples were coated with a thin film of gold to prevent surface changing and to protect the surface material from thermal damage by the electron beam.

2.3. Synthesis

2.3.1. Polymer–anchored 2-(α-hydroxymethyl)-benzimidazole (PS-Hhmbmz, I)

Chloromethylated polystyrene (3.0 g) was allowed to swell in DMF (40 ml) for 2 h. A DMF solution (30 ml) of 2-(α-hydroxymethyl)benzimidazole (1.332 g, 9 mmol) was added to the above suspension followed by triethylamine (4.50 g) in ethylacetate (100 ml). The reaction mixture was heated under reflux while stirring for 8 h. After cooling to room temperature, the creamish yellow resin was filtered off, washed thoroughly with hot DMF followed by hot ethanol and dried in an oven in air at 120 °C.

2.3.2. Preparation of PS-[Cu(hmbmz)$_2$] 1

Polymer anchored ligand PS-Hhmbmz (1.5 g) was allowed to swell in DMF (20 ml) for 2 h. A DMF solution (10 ml) of cupric acetate monohydrate (0.798 g, 4 mmol) was added to the above suspension and the reaction mixture was heated at 90 °C in an oil bath with stirring for 6 h. After cooling it was suction filtered, washed with hot DMF and again suspended in DMF (20 ml). Hhmbmz (0.592 g, 4 mmol) was added to the above suspension and further heated at 90 °C in an oil bath with stirring for 4 h. The polymer-anchored copper complex thus obtained was filtered, washed with hot DMF followed by hot ethanol several times and dried in an oven in air at 120 °C.

2.3.3. Preparation of PS-[VO(hmbmz)$_2$] 2

Polymer-anchored PS-[VO(hmbmz)$_2$] was prepared following the above procedure using PS-Hhmbmz (1.5 g), VOSO$_4$ · 5H$_2$O (1.01 g, 4 mmol) and Hhmbmz (0.592 g, 4 mmol). The grayish polymer-anchored vanadium complex was dried at 120 °C in an oven in air.

2.3.4. Preparation of PS-[MoO$_2$(hmbmz)$_2$] 3

Polymer-anchored ligand PS-Hhmbmz (1.5 g) was allowed to swell in DMF (20 ml) for 2 h. [MoO$_2$(acac)$_2$] (1.39 g, 4 mmol) was added to the above suspension and the reaction mixture was heated in an oil bath for 6 h while stirring. After cooling the yellow resin was suction filtered, washed with hot DMF and again suspended in DMF (20 ml). To this was added Hhmbmz (0.592 g, 4 mmol) and further heated at 90 °C in an oil bath while stirring for 4 h. The polymer-anchored complex thus obtained was filtered, washed with hot DMF followed by hot ethanol and dried at 120 °C in an oven in air.

2.3.5. Preparation of [Cu(hmbmz)$_2$]

A filtered methanolic solution of cupric acetate (0.40 g, 2 mmol in 10 ml) was added to the methanolic solution of Hhmbmz (0.592 g, 4 mmol in 10 ml) and the reaction mixture was refluxed on a water bath for 6 h. After cooling the reaction mixture to room temperature, the separated coloured solid was filtered off, washed with methanol and dried at 120 °C in an oven in air. Yield: 60%.

2.3.6. Preparation of [VO(hmbmz)$_2$]

VOSO$_4 \cdot$ 5H$_2$O (0.506 g, 2 mmol) was dissolved in 2 ml water and 5 ml methanol and filtered. This solution was added to a methanolic solution of Hhmbmz (0.592 g, 4 mmol in 10 ml) and the reaction mixture was refluxed on a water bath for 5 h. After reducing the volume of the solvent to ca. 5 ml, it was kept at 10 °C overnight whereupon a gray solid separated out which was filtered, washed with cold methanol and dried at 120 °C in an oven in air. Yield: 40%.

2.3.7. Preparation of [MoO$_2$(hmbmz)$_2$]

Hhmbmz (0.592 g, 4 mmol) was dissolved in 20 ml methanol and to this [MoO$_2$(acac)$_2$] (0.662 g, 2 mmol) was added in portions with vigorous shaking to dissolved the solid. After filtering, the resulting solution was refluxed on a water bath for 8 h. The volume of the solvent was reduced to ca. 10 ml and kept at 10 °C overnight whereupon an yellow solid precipitated out, which was filtered, washed with methanol and dried in an oven in air at 120 °C. Yield: 60%.

2.4. Catalytic activity studies

2.4.1. Oxidation of styrene

PS-[Cu(hmbmz)$_2$] and PS-[VO(hmbmz)$_2$] catalysts were used to carry out the epoxidation of styrene where these were swelled in acetonitrile for 12 h prior to their use in the reaction. Styrene (1.0 g, 0.0096 mol) and aqueous 30% H$_2$O$_2$ (4.0 g, 0.0096 mole) were mixed in 20 ml acetonitrile and the reaction mixture was heated with continuous stirring in an oil bath maintained at 60 °C. An appropriate catalyst (0.10 g) was added to the reaction mixture and stirred for 6 h. The progress of reaction was monitored by withdrawing samples at different time intervals and analysing them by a gas chromatograph (Shimadzu 14 B FID Detector, SE-52 packed column). The identities of the products were confirmed by GC-MS (Shimadzu GC-MS QP 5000).

2.4.2. Oxidation of ethyl benzene

PS-[Cu(hmbmz)$_2$] and PS-[VO(hmbmz)$_2$] catalysts were used to carry out the oxidation of ethyl benzene where these were swelled in acetonitrile as stated above. Oxidation of ethyl benzene was carried out similarly as mentioned for styrene using ethyl benzene (0.316 g, 0.0029 mol), 70% *tert*-butyl-hydroperoxide (TBHP) (1.15 g, 0.008 mol) and catalyst (0.050 g) in 10 ml acetonitrile at 60 °C. The effect of various parameters such as swelling time in acetonitrile, temperature and different oxidants were taken into consideration in order to study their effect on the reaction. However, basic procedure was the same as outlined above.

2.4.3. Oxidative bromination of salicylaldehyde using PS-[VO(hmbmz)$_2$] and PS-[MoO$_2$(hmbmz)$_2$]

In a typical reaction, salicylaldehyde (0.244 g, 0.002 mol) was added to an aqueous solution (4 ml) of KBr (0.5 g, 4 mmol) followed by aqueous 30% H$_2$O$_2$ (1.93 g, 15 mmol) in a 50 ml reaction flask. An appropriate catalyst (0.02 g) and 70% HClO$_4$ (0.1 ml) were added to it and the reaction was considered to begin with stirring. Additional 3 mmol of 70% HClO$_4$ was added to the reaction mixture in three equal portions at every half an hour interval with stirring. After 4 h, the separated white product was filtered, washed with water followed by diethyl ether and dried in air. The crude mass was recrystallized from CH$_2$Cl$_2$. The identity of the product was confirmed by GC–MS analysis.

3. Results and discussion

3.1. Synthesis

Miller and Sherrington [34] have shown that 2-(2-pyridyl)imidazole can be anchored onto polystyrene, through covalent attachment of imine nitrogen, by the reaction of ligand and chloromethylated polystyrene in refluxing toluene. We have modified the procedure by using triethylamine as chlorine abstracting agent to facilitate the reaction [35]. Thus, reaction of chloromethylated polystyrene, cross linked with 5% divinylbenzene, with 2-(α-hydroxymethyl)benzimidazole in DMF in presence of triethylamine leads to the formation of polymer anchored ligand PS-Hhmbmz. During this process, the NH group of benzimidazole reacts with –CH$_2$Cl group as shown in Scheme 2.
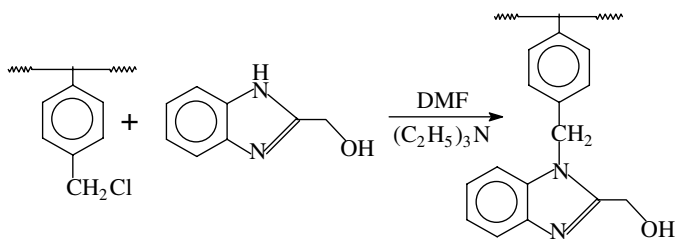
Scheme 2.

The remaining chlorine content of 1.95% (0.5 mmol Cl per gram of resin) in anchored ligand suggests roughly 90.6% conversion with respect to the available chloromethyl groups. This anchored ligand on reaction with cupric acetate possibly gives an acetate coordinated complex [35], which in the presence of 2-(α-hydroxymethyl)benzimidazole gives complex PS-[Cu(hmbmz)$_2$] as shown in Scheme 3. Similarly, complexes PS-[VO(hmbmz)$_2$] and PS-[MoO$_2$(hmbmz)$_2$] can be prepared from VO(SO$_4$)$_2$ and [MoO$_2$(acac)$_2$], respectively, in presence of Hhmbmz. Tembe and co-workers [36,37] have proposed coordination of O and N atoms from two amino acids appended in the same

PS-[Cu(hmbmz)$_2$] (1)

PS-[VO(hmbmz)$_2$] (2)

PS-[MoO$_2$(hmbmz)$_2$] (3)
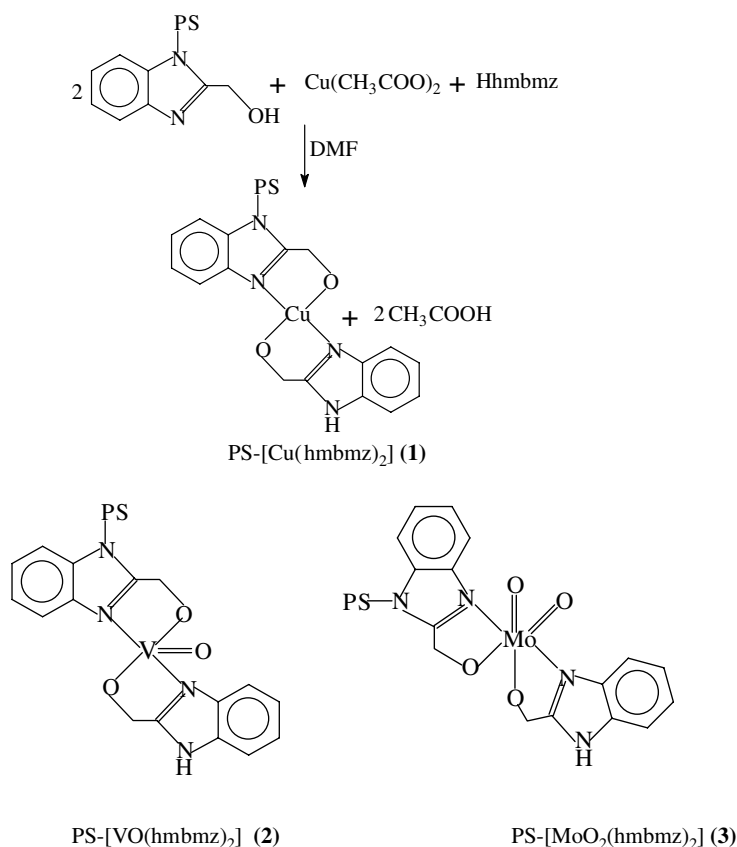
Scheme 3. Proposed structures for complexes and reaction scheme for the preparation of complex PS-[Cu(hmbmz)$_2$], where PS represents polystyrene backbone.

polymeric chain of polystyrene in PS-[Ru(L$_2$)Cl$_2$]Cl and PS-[CuL$_2$] (where PS-HL = L-phenyl alanine or L-valine supported on polystyrene). As appended ligands will be little away from each other in a polymeric chain of polystyrene, the procedure adopted here would favor the formation of anchored complex at each appended ligand and such process has been reported in the literature [38]. The proposed structures of oxovanadium(IV) and dioxomolybdenum(VI) complexes are also presented in Scheme 3. Further, as neat dioxomolybdenum(VI) complex of 2-(α-hydroxymethyl)benzimidazole was reported to have *cis*-[MoO$_2$]$^{2+}$ structure [39], the two oxo groups in molybdenum complex have been shown having *cis* position. The corresponding neat complexes of these metal ions have also been isolated to compare their catalytic activity.

3.2. Characterization

The analytical data of the anchored-complexes presented in Table 1 shows the formation of complexes while metal and ligand loading (Table 2) suggest metal to ligand stoichiometry to be 1:2. Catalysts **1** and **2** are thermally stable up to 230 °C, while **3** starts decomposing at 180 °C. However, decomposition patterns of all catalysts are nearly similar. The decomposition patterns of complexes and polymer backbone are not distinguishable and this is understandable because neat metal complexes of Hhmbmz are even expected to decompose completely at higher temperature [39,40]. In the range up to 560 °C, these catalysts exothermically decompose completely in multiple steps to give CuO, V$_2$O$_5$ and MoO$_3$ as final residues.

Table 2
Ligand loading, metal ion loading and ligand: metal ratio data

Compound	Ligand loading (mmol g^{-1} of resin)	Metal ion loading[a] (mmol g^{-1} of resin)	Ligand:metal ratio
PS-Hmbmz	1.95		
PS-[Cu(hmbmz)$_2$]	0.91	0.56	1.62:1
PS-[VO(hmbmz)$_2$]	0.86	0.57	1.52:1
PS-[MoO$_2$(hmbmz)$_2$]	0.72	0.46	1.56:1

[a] Metal ion loading $= \frac{\text{Observed metal } \% \times 10}{\text{Atomic weight of metal}}$.

Scanning Electron Micrographs (SEM) for single bead of pure chloromethylated polystyrene, anchored-ligand and complexes were recorded to understand the morphological changes occurring at various stages and some of the images are presented in Fig. 1. As expected pure polystyrene bead has smooth and flat surface while anchored ligand and complexes show very slight roughening of the top layer. Accurate information on the morphological changes in terms of exact orientation of ligands coordinated to the metal ion has not been possible due to poor loading of the metal complexes.

3.2.1. IR spectral studies

The NH stretching band of Hhmbmz occurs at 2630–2825 cm^{-1} as a broad feature which indicates the presence of strong hydrogen bonding possibly between the hydrogen of the NH group and the oxygen of the alcohol [39]. A broad band at 3400 cm^{-1} is due to the hydroxyl group. On anchoring with polystyrene, the broad feature of NH disappears suggesting the covalent bond formation after reaction between –NH of ligand and –CH$_2$Cl of polystyrene. At the same time, several bands of medium intensity appear at 2800–
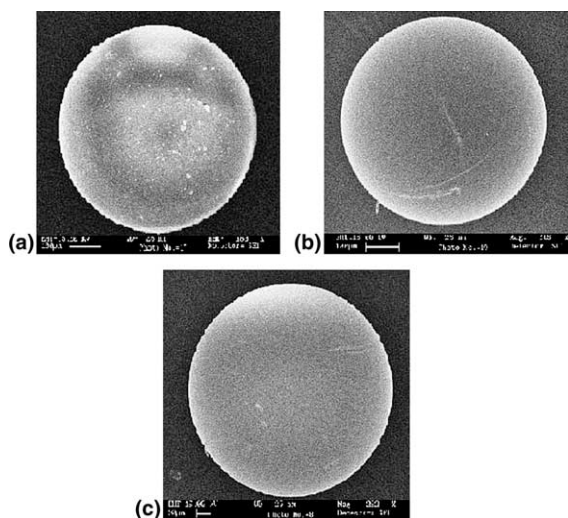
Table 1
Physical and analytical data of the polymer-anchored ligand and complexes

S. No.	Compound	Colour	Found (%)			
			C	H	N	M
1	PS-Hmbmz, **I**	Yellow	66.83	8.54	5.46	
2	PS-[Cu(hmbmz)$_2$], **1**	Green	60.40	8.01	5.10	3.56
3	PS-[VO(hmbmz)$_2$], **2**	Grey	61.80	7.49	4.86	2.90
4	PS-[MoO$_2$(hmbmz)$_2$], **3**	Yellow	64.06	7.81	4.02	4.42

Fig. 1. Scanning electron micrographs of (a) chloromethylated polystyrene, (b) PS-Hhmbmz and (c) PS-[Cu(hmbmz)$_2$].

Table 3
Electronic spectral data

Compound	Solvent	λ_{max}/nm
Hhmbmz	Methanol	276, 283
PS-[Cu(hmbmz)$_2$]	Reflectance	243, 521
PS-[VO(hmbmz)$_2$]	Reflectance	245, 495
PS-[MoO$_2$(hmbmz)$_2$]	Reflectance	249, 338, 430

2985 cm^{-1} due to the presence of CH$_2$ group of polystyrene. In addition, all characteristic bands due to free ligand including a relatively stronger band at 3400 cm^{-1} due to v(OH) also appear. In polymer-anchored metal complexes all these characteristic bands also appear but coordination of ligand to metal cannot be inferred unequivocally due to complexity in the spectral features. However, presence of several bands in the 400–500 cm^{-1} region in all complexes should suggest the coordination of oxygen and nitrogen of the ligand to the metal. Other characteristics bands, for example, v(V=O) at 985 cm^{-1} in PS-[VO(hmbmz)$_2$] and v_{sym}(O=Mo=O) and v_{asym}(O=Mo=O) at 901 and 944 cm^{-1} in PS-[MoO$_2$(hmbmz)$_2$] suggest the presence of vanadium and molybdenum in the coordination sphere.

3.2.2. Electronic spectral studies

Table 3 represents electronic spectral data of free ligand Hhmbmz and polymer-anchored complexes. Spectrum of the Hhmbmz was recorded in methanol while diffused reflectance spectra (DRS) were recorded for the complexes. The UV–Vis spectrum of ligand exhibits two intense bands in methanol at 276 and 283 nm due to $\pi \to \pi^*$ and $n \to \pi^*$ transitions, respectively. In

the reflectance spectra of complexes at least one band could be located at ca. 245 nm which is assigned to the $\pi \to \pi^*$ transition. Another band at 338 nm is only visible in dioxomolybdenum(VI) and this may be assigned to $n \to \pi^*$ transition. In addition, all complexes exhibit one band in the visible region. In case of copper(II) and oxovanadium(IV) complexes, this may be considered due to d–d transition as they have one unpaired electron in d-orbital. In dioxomolybdenum(VI), this band is due to ligand to metal charge transfer band from highest occupied p-orbital of the ligand to the empty d-orbital of molybdenum. All these data are consistent with the coordination of metal ion with polymer-anchored ligand. No bands could be located in the visible region.

3.2.3. EPR studies

Room temperature X-band EPR spectra of the neat [Cu(hmbmz)$_2$] compound and polymer-anchored complex PS-[Cu(hmbmz)$_2$] are reproduced in Fig. 2. The spectrum of the neat copper complex exhibits a broad signal due to the large dipolar coupling with its neighboring units which is typical of a condensed molecule and thereby no hyperfine features could be identified. However, for the polymer-anchored copper compound, PS [Cu(hmbmz)$_2$], the EPR spectrum shows an axial pattern with resolved hyperfine features in the parallel region but the perpendicular hyperfine components are not resolved. The resolved EPR pattern of the polymer-anchored sample is an indication that the copper centers are well dispersed in the polymer matrix. The simulation of EPR spectrum of PS-[Cu(hmbmz)$_2$] was carried to extract the following Hamiltonian parameters: $g_\| = 2.27$, $g_\perp = 2.065$, $A_\| = 156$ G and the microwave frequency was 9.4505 GHz. The hyperfine lines are due to the interaction of paramagnetic
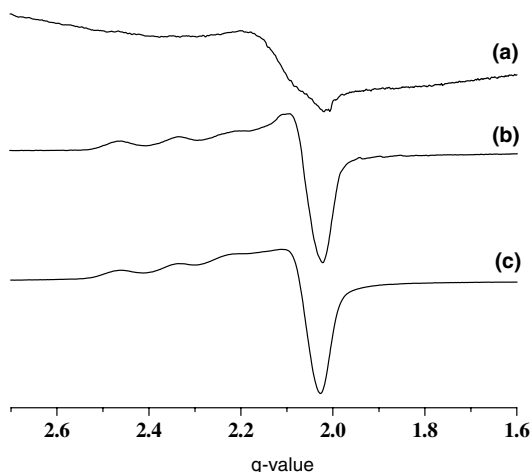
Fig. 2. Room temperature X-band EPR spectra of (a) neat [Cu(hmbmz)$_2$], (b) fresh PS-[Cu(hmbmz)$_2$] and (c) recovered PS-[Cu(hmbmz)$_2$].

Fig. 3. Room temperature X-band EPR spectra of (a) neat [VO(hmbmz)$_2$], (b) fresh PS-[VO(hmbmz)$_2$] and (c) recovered PS-[VO(hmbmz)$_2$].

Cu(II) center with d^9 electronic configuration with its own nucleus (Cu, $I = 3/2$). The parameters are characteristic of a copper complex with pentagonal geometry. After catalytic reaction, the catalyst PS-[Cu(hmbmz)$_2$ was recovered and its EPR spectrum was recorded. The EPR spectra of both fresh and recovered catalyst were similar with identical Hamiltonian parameters. The latter observation is an indication that the environment and coordination geometry of copper ion of the PS-[Cu(hmbmz)$_2$] compound was not altered during the reaction.

Similar to the copper compounds, X-band EPR spectra of neat and polymer anchored vanadium compounds namely [VO(hmbmz)$_2$] and PS-[VO(hmbmz)$_2$] were recorded at room temperature and are shown in Fig. 3. The EPR spectrum for the neat compound was broad and not well resolved enough to extract the EPR Hamiltonian parameters. The broad hyperfine feature should be due to the dipolar interactions with the neighboring units. However, PS-[VO(hmbmz)$_2$], shows resolved hyperfine features with axial symmetry and the Hamiltonian parameters: $g_\parallel = 1.94$, $A_\parallel = 188$ G, $g_\perp = 1.991$, $A_\perp = 66$ G, and $v_{mw} = 9.4515$ GHz The hyperfine lines are typical for an interaction of the unpair electron of vanadium (IV) ion with its nucleus (^{51}V, $I = 7/2$). The anisotropic EPR spectrum of V(IV) ion with $g_\parallel < g_\perp$ and $A_\parallel > A_\perp$
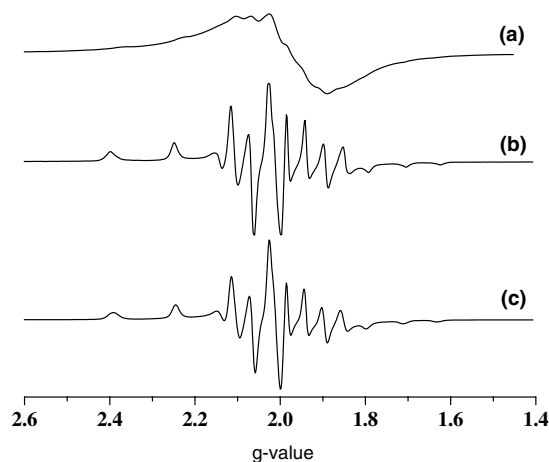
is characteristic of square pyramidal complexes with possible C_4V symmetry where V=O bond is along the z-axis and the other four coordinating atoms are along the x- and y-axes. The well resolved hyperfine features reflect the fact that the vanadium centers are well dispersed with the polymer back-bones. After carrying out the catalytic reactions, the polymer anchored catalyst, PS-[VO(hmbmz)$_2$], was filtrated, washed and dried and its EPR spectrum was recorded under identical conditions. The spectra of both the fresh catalyst and the spent catalyst were identical and thus the Hamiltonian parameters. These observations can be explained in a similar manner as explained for PS-[Cu(hmbmz)$_2$], i.e., the environment and coordination geometry of the PS-[VO(hmbmz)$_2$] compound was intact during the reaction. Thus, validating the point of perfect heterogenization.

3.3. Catalytic activity

3.3.1. Oxidation of styrene

PS-[Cu(hmbmz)$_2$] and PS-[VO(hmbmz)$_2$] catalysts tested for the oxidation of styrene gave styrene oxide, benzaldehyde and benzoic acid as major products along with small amount of unidentified products. In an optimized condition, styrene (1.0 g, 9.6 mmol), 30% aqueous H$_2$O$_2$

Table 4
Percentage conversion of styrene, product selectivity and TOF[a]

| Catalyst (wt.)	Time (h)	Convn. (%)	TOF[b]	Products selectivity (%)			
				Styrene oxide	Benzaldehyde	Benzoic acid	Others
PS-[Cu(hmbmz)$_2$] (0.1 g)	3	32.3	18.5	14.5	68.7	8.5	8.3
	6	37.0		12.6	57.6	14.6	15.2
[Cu(hmbmz)$_2$] (0.006 g)	3	31.2	17.9	17.0	70.0	6.5	6.5
	6	41.7		16.2	64.9	9.7	9.2
PS-[VO(hmbmz)$_2$] (0.1 g)	3	25.0	14.3	2.7	97.3	3.1	–
	6	48.3		4.4	78.6	–	13.9
[VO(hmbmz)$_2$] (0.0104 g)	3	2.5	1.5	–	82.0	–	18.0
	6	4.4		–	75.0	–	25.0

[a] Reaction condition: styrene (1.0 g, 0.0096 mol), 30% H$_2$O$_2$ (4.0 g, 0.0096 mol), temperature 60 °C, 20 ml CH$_3$CN, catalyst amount as shown in table. Swelling time: 12 h in CH$_3$CN.
[b] TOF: turn over frequency – moles of substrate converted per mole of metal (in solid catalyst) per hour.

(4.0 g, 9.6 mmol) and catalyst (0.1 g) in 20 ml CH$_3$CN at 60 °C gave 37.0% (with PS-[Cu-(hmbmz)$_2$]) and 48.3% (with PS-[VO(hmbmz)$_2$]) conversions of styrene in 6 h of reaction time (Table 4). Amongst the three major products, the selectivity varied in the order: benzaldehyde (57.6%) > benzoic acid (14.6%) > styrene oxide (12.6%) (for PS-[Cu(hmbmz)$_2$]) while benzaldehyde (78.3%) > styrene oxide (4.4%) > benzoic acid (3.1%) for PS-[VO(hmbmz)$_2$]. Though, both the catalysts are selective towards the formation of benzaldehyde, PS-[VO(hmbmz)$_2$] is more selective than PS-[Cu(hmbmz)$_2$]. The performances of both the catalysts have also been compared with the corresponding neat complexes and the pertinent data are also presented in Table 4. The activity of neat complex [Cu(hmbmz)$_2$] is comparable in the performance while [VO(hmbmz)$_2$] gives only 4.4% conversion of styrene in 6 h of reaction time. However, it exclusively gives benzaldehyde.

3.3.2. Oxidation of ethyl benzene

Generally oxidation of ethyl benzene gives three major products, acetophenone, benzaldehyde and styrene (Scheme 4). The catalysts PS-[Cu(hmbmz)$_2$] and PS-[VO(hmbmz)$_2$] also catalyse the oxidation of ethyl benzene to acetophenone with 97% selectivity under mild conditions. Reaction conditions were optimized for maximum oxidation by varying temperature, oxidants and
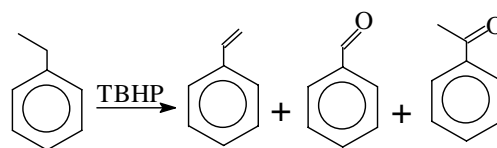
Scheme 4.

swelling time of catalysts in CH$_3$CN considering PS-[Cu(hmbmz)$_2$] as catalyst.

3.3.3. Effect of different oxidants

Oxidation of ethyl benzene was carried out using different oxidants viz 70% of TBHP, 30% H$_2$O$_2$, NaOCl and *m*-chloro perbenzoic acid. In a typical reaction conditions ethyl benzene (0.316 g, 2.9 mmol), catalyst PS-[Cu(hmbmz)$_2$] (50 mg) and oxidant (8 mmol) in 10 ml CH$_3$CN were taken in a reaction flask and stirred at 60 °C. The reaction products were analyzed at 3 and 6 h of reaction time. No conversion of ethyl benzene was found with NaOCl and *m*-chloro perbenzoic acid while TBHP and H$_2$O$_2$ gave 43.5% and 60.8% conversion, respectively, in 6 h. However, selectivity to acetophenone is 96.6% with TBHP where it is only 66.5% with H$_2$O$_2$. The relevant data are summarized in Table 5. Thus, TBHP can be considered as more selective oxidant amongst the oxidants studied.

Table 5
Effect of various oxidant on the oxidation of ethyl benzene using PS-[Cu(hmbmz)$_2$][a]

Oxidant	Reaction time (h)	% Convn.	TOF	Products (mol%)	
				Acetophenone	Others
TBHP (70%)	3	38.1	13.09	94.9	5.1
	6	43.5		96.6	3.4
H$_2$O$_2$ (30%)	3	58.7	20.71	67.9	32.1
	6	60.8		66.6	33.4
NaOCl	3	No reaction			
	6	No reaction			
m-Chloro per benzoic acid	3	No reaction			
	6	No reaction			

[a] Reaction conditions: ethyl benzene (2.9 mmol), oxidant (8 mmol), catalyst (50 mg), CH$_3$CN (10 ml) and temperature (60 °C).

3.3.4. Effect of swelling time

Swelling is an important property of any polymer-anchored catalyst as it makes easy approach of substrate to the catalytic centre. We have studied the effect of swelling time in acetonitrile and data are presented in Table 6. Three different swelling durations (3, 6 and 12 h) were considered while keeping other parameters fixed as mentioned above and reaction products were analyzed at 3 and 6 h reaction time. It is clear from the data that 6 h swelling period is the best one to get good result. Swelling for 12 h has really no effect either in terms of conversion or in terms of selectivity of the formation of acetophenone.

3.3.5. Effect of temperature

Effect of temperature on the catalytic performance has been studied at three different tempera-tures (50, 60 and 70 °C), while keeping ethyl benzene (2.9 mmol), TBHP (8 mmol) and catalyst (50 mg) in 10 ml of CH$_3$CN. The percent conversion and product selectivity data are presented in Table 7. It is clear from the data that the temperature has basically no effect on the ethyl benzene conversion and reaction can be performed at temperatures between 50 and 70 °C. However, reduction in selectivity to acetophenone is observed, which could be due to the faster decomposition of TBHP and formation of some byproducts.

3.3.6. Comparison of catalytic activity with PS-[VO(hmbmz)$_2$] and neat complexes

Under the optimized reaction conditions PS-[VO(hmbmz)$_2$] showed poor catalytic activity where the conversion was only 2.5% though acetophenone was the only product. Catalytic perfor-

Table 6
Effect of swelling time in CH$_3$CN on the oxidation of ethyl benzene using PS-[Cu(hmbmz)$_2$][a]

Swelling duration (h)	Reaction time (h)	% Convn.	TOF	Products (mol%)	
				Acetophenone	Others
3	3	22.3	7.7	92.3	7.7
	6	35.4		93.3	6.7
6	3	38.1	13.09	94.9	5.1
	6	43.5		96.6	3.4
12	3	30.8	10.7	88.8	11.2
	6	41.7		97.0	3.0

[a] Reaction conditions: ethyl benzene (2.9 mmol), TBHP (8 mmol), catalyst (50 mg), CH$_3$CN (10 ml) and temperature (60 °C).

Table 7
Effect of temperature on the oxidation of ethyl benzene using PS-[Cu(hmbmz)$_2$][a]

| Reaction Temperature (°C)	Reaction time (h)	% Convn.	TOF	Products (mol%)	
				Acetophenone	Others
50	3	22.2	14.28	96.9	3.1
	6	41.9		97.1	2.9
60	3	38.1	13.09	94.9	5.1
	6	43.5		96.6	3.4
70	3	37.8	13.09	95.6	4.4
	6	42.8		93.5	6.5

[a] Reaction conditions: ethyl benzene (2.9 mmol), TBHP (8 mmol), catalyst (50 mg) and CH$_3$CN (10 ml).

mance of PS-[Cu(hmbmz)$_2$] under the above conditions was also compared with neat [Cu(hmbmz)$_2$]. The relevant data are presented in Table 8. To our surprise, 50 mg of neat complex has similar catalytic efficiency. However, TOF is much less in comparison to polymer anchored one. Further, easy recovery of the anchored catalyst and the recyclability make it better catalyst. Thus, PS-[Cu-(hmbmz)$_2$] is better catalyst than PS-[VO(hmbmz)$_2$] for the oxidation of ethyl benzene with high selectivity towards acetophenone. Catalytic performance of [VO(hmbmz)$_2$] was not attempted as respective polymer supported catalyst itself gave a poor result.

3.3.7. Oxidative bromination of salicylaldehyde by PS-[VO(hmbmz)$_2$] and PS-[MoO$_2$(hmbmz)$_2$]

Enzymes vanadate-dependent haloperoxidases and models of their active centre catalyse the oxidative halogenation of hydrocarbon (Eq. (1)), and the oxidation of organic (prochiral) sulfides to (chiral) sulfoxides (Eq. (2)) [41–44]. Similar oxidation has also been achieved by PS-[VO(hmbmz)$_2$] and PS-[MoO$_2$(hmbmz)$_2$]. We observed that both the catalysts catalysed the oxidative bromination of salicylaldehyde, using H$_2$O$_2$/KBr in presence of HClO$_4$ in aqueous solution (Eq. (3)).

$$Hal^- + H_2O_2 + RH + H^+ \rightarrow RHal + 2H_2O \quad (1)$$

$$RSR' + H_2O_2 \rightarrow RS(O)R' + H_2O \quad (2)$$

$$(3)$$
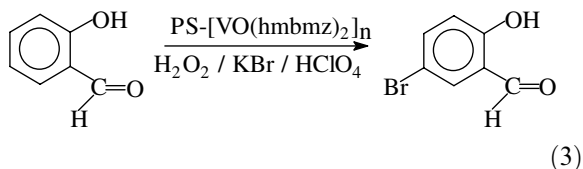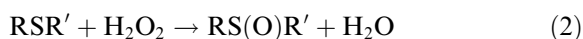
In order to optimize the reaction conditions, concentrations of HClO$_4$ and H$_2$O$_2$ were varied for the fixed amount of substrate (0.61 g, 5 mmol), catalyst (50 mg), KBr (1.20 g, 10 mmol) in 10 ml of water for both the catalysts. At least 15 mmol of 70% HClO$_4$ and 15 mmol H$_2$O$_2$ for 5 mmol of substrate (i.e., 1:3 molar ratio each)

Table 8
Comparison of catalytic activity of PS-[Cu(hmbmz)$_2$], PS-[VO(hmbmz)$_2$] and neat [Cu(hmbmz)$_2$] for the oxidation of ethyl benzene

Catalyst	Reaction time (h)	% Convn.	TOF	Products (mol%)	
				Acetophenone	Others
PS-[Cu(hmbmz)$_2$]	3	38.1	13.1	94.9	5.1
	6	43.5		96.6	3.4
[Cu(hmbmz)$_2$]	3	32.9	11.3	98.3	1.7
	6	42.4		95.2	4.8
PS-[VO(hmbmz)$_2$]	3	2.0		100	–
	6	2.5		100	–

were found to be the best conditions to give 100% conversion of salicylaldehyde to 5-bromosalicylal-dehyde selectively. Addition of $HClO_4$ at a time causes slow decomposition of catalyst. However, this decomposition could be stopped if $HClO_4$ is successively added in portions. Further, polymer support serves as protein mantle and its inertness towards $HClO_4$ provides extra stability to the complexes during catalytic activity study. Both catalysts were tested for three continuous cycles without loss in its activity, which suggest their reusability.

3.3.8. Test for heterogeneity of reaction

In order to check, leaching of the metal complex from the polymer-anchored catalyst into reaction medium during the oxidation reactions, separate experiments were carried in a few selected systems. The reaction mixture after a contact time of 6 h was filtered and the poly-mer-anchored catalyst was separated. The filtrate collected was placed into the reactor and the reaction was continued by adding fresh oxidant for another 3 h. The gas chromatographic analy-sis of the reaction mixture showed no further in-crease in the conversion. This confirms that the reaction did not proceed on the removal of the solid catalyst and hence the reaction was hetero-geneous. In addition to this, filtrate was tested by ICP-OES for the presence of any leached metal and it showed the absence of Cu in the filtrate.

Further, the recyclability experiments were performed by separating the catalysts from the reaction mixture after a contact time of 6 h. The catalyst separated was washed with acetoni-trile, dried and subjected to another cycle with a fresh reaction mixture, under the same reaction conditions. It was found that the conversion was nearly the same. The above procedure was repeated for three cycles with the anchored cata-lysts, and we did not observe any loss in the cat-alytic activity of the anchored catalyst. The ESR spectra (Figs. 2 and 3) of the spent catalysts also support the fact that copper and vanadyl centres are intact and the coordination environments were not altered after the catalytic run with H_2O_2.

4. Conclusions

PS-[Cu(hmbmz)$_2$] PS-[VO(hmbmz)$_2$] and PS-[MoO$_2$(hmbmz)$_2$] polymer-anchored complexes having potential catalytic activities for the oxida-tion of styrene and ethylbenzene and oxidative bro-mination of salicylaldehyde have been prepared and characterized. Oxidation of styrene gives three products, styrene oxide, benzaldehyde and benzoic acid using PS-[Cu(hmbmz)$_2$] and PS-[VO(hmbmz)$_2$] as catalysts where benzaldehyde being the major product. Catalysts PS-[Cu(hmbmz)$_2$] was highly selective for the oxidation of ethylbenzene to acetophenone. PS-[VO(hmbmz)$_2$] and PS-[MoO$_2$-(hmbmz)$_2$] are active and selective in the oxidative bromination of salicylaldehyde. All these polymer-anchored catalysts are better than that of the corre-sponding neat complexes. These catalysts do not leach in any of the above catalytic reaction and are heterogeneous in nature. They are recyclable up to three cycles without loss in their catalytic activities.

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