

Polymer-anchored vanadium(IV), molybdenum(VI) and copper(II) complexes of bidentate ligand as catalyst for the liquid phase oxidation of organic substrates

Mannar R. Maurya*, Maneesh Kumar, Umesh Kumar

Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India

Received 2 March 2007; received in revised form 25 March 2007; accepted 26 March 2007

Available online 6 April 2007

Abstract

Monobasic bidentate ligand 2-(2'-hydroxyphenyl)benzimidazole (Hhpbmz) has been covalently bonded to the chloromethylated polystyrene cross-linked with 5% divinylbenzene. Treatment of the resulted chelating resin, abbreviated as PS-Hhpbmz, with [VO(acac)₂], [MoO₂(acac)₂] (Hacac = acetylacetonate) and Cu(CH₃COO)₂·H₂O, gave polymer-anchored complexes PS-[VO(hpbmz)₂], PS-[MoO₂(hpbmz)₂] and PS-[Cu(hpbmz)₂], respectively. The corresponding neat complexes with Hhpbmz have also been prepared similarly. Structures of these complexes have been established on the basis of elemental analyses, scanning electron micrographs and spectroscopic (infrared and electronic) as well as thermogravimetric studies. These complexes have been tested as catalyst for the oxidation of styrene, ethylbenzene and methyl phenyl sulfide. Reaction conditions for the maximum oxidation of these substrates have been optimised by considering the concentration of oxidant, amount of catalyst, volume of solvent and temperature of the reaction mixture. Under the optimised conditions styrene gave a maximum of 58.9% conversion with five reaction products namely styrene oxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid, and phenylacetaldehyde. Oxidation of ethylbenzene gave 47.7% conversion where benzaldehyde, phenyl acetic acid, styrene, 1-phenylethane-1,2-diol and benzoic acid have been obtained as major oxidation products. A maximum of 76.5% conversion of methyl phenyl sulfide, catalysed by PS-[VO(hpbmz)₂], has been achieved. Catalyst, PS-[MoO₂(hpbmz)₂] has shown comparable (75.1%) catalytic activity while only 44.8% conversion has been achieved with PS-[Cu(hpbmz)₂]. Irrespective of their catalytic performances, the selectivity for the formation of sulfoxide is almost similar (ca. 75%) for all these catalysts. These catalysts do not leach metal ions during catalytic activity and are recyclable.

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Keywords: Polymer-anchored complexes; Catalysts; Vanadium complexes; Molybdenum complexes; Oxidation reactions

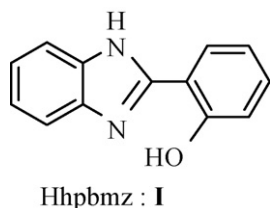
1. Introduction

Immobilisation of the homogeneous catalysts through covalent bonding with polymer support is one of the most specialized methods amongst the reported heterogenization of homogeneous catalysts because polymer support enhances the thermal stability, selectivity, recyclability and easy separation of the catalyst from reaction products leading to the operational flexibility [1,2]. Amongst polymer supports, chloromethylated polystyrene cross linked with divinylbenzene is one of the most widely employed macromolecular supports for heterogenization of homogeneous catalysts [3–8]. Depending upon the metal

centres of the heterogeneous catalysts, these can be used as oxidation or reduction catalysts [9–12]. Review article by Laedbeater and Marco and references mentioned therein reflects the importance of supported complexes in organic synthesis and catalysis [13].

In the present investigation, we report the isolation and characterisation of oxovanadium(IV), dioxomolybdenum(VI) and copper(II) complexes of polymer-anchored bidentate ligand, 2-(2'-hydroxyphenyl)benzimidazole (Hhpbmz, **I**) (Scheme 1). Catalytic potential of these anchored complexes has been tested for the oxidation of styrene and ethylbenzene. Selective oxidation of styrene has been carried out using various homogeneous catalysts e.g. metal complexes [14–18] and supported heterogeneous catalysts such as mixed metal oxides [19], zeolites [20], zeolite encapsulated metal complexes [21], metal complexes supported on mesoporous materials, etc. [22,23]. For

* Corresponding author. Tel.: +91 1332 285327; fax: +91 1332 273560.
E-mail address: rkmanfyc@iitr.ernet.in (M.R. Maurya).



Scheme 1.

the oxidation of ethylbenzene, homogeneous catalysts such as metal acetylacetonates [24,25], [Co(2-pyridinecarboxamide)₃] [26], metalloporphyrins [27,28], macrocyclic complexes [29] etc. as well as heterogeneous catalysts such as metal complex supported on alumina/silica [30], heteropolyacids [31], M–APO-11 (M=Co, Mn and V) [32], Mn–MCM-41 [33], polymer-anchored complexes [34], zeolite encapsulated metal complexes [35], etc. have been employed.

Oxidation of sulfides (thioethers) to sulfoxides (sulfoxidase activity), exhibited by enzymes vanadate-dependent haloperoxidases, has been considered as one of the important catalytic reactions [36–38]. Several vanadium and molybdenum complexes model this reaction [39,40] but only limited literature cites the use of polymer supported vanadium and molybdenum complexes for the oxidation of sulfides [41]. We have, therefore, also tested the catalytic ability of these polymeric-supported complexes for the oxidation of methyl phenyl sulfide.

2. Experimental

2.1. Materials and characterisation procedures

V₂O₅, ammonium heptamolybdate (S.D. fine chemicals, India), cupric acetate monohydrate, salicylic acid, ethylbenzene (Loba Chemie, India), methyl phenyl sulfide, polyphosphoric acid, styrene (Acros Organics, USA) and acetylacetone (E. Merck, India) were used as obtained. Chloromethylated polystyrene [18.9% Cl (5.3 mmol Cl per gram of resin) cross-linked with 5% divinylbenzene] was generously supplied by Thermax Limited, Pune, India. [VO(acac)₂] [42] and [MoO₂(acac)₂] [43] were prepared according to the methods reported in the literature.

Elemental analyses of the compounds were carried out on an Elementar model Vario-EI-III. IR spectra were recorded as KBr pellets on a Nicolet NEXUS Aligent 1100 series FT-IR spectrometer. Electronic spectra of ligand and complexes were recorded in Nujol on a Shimadzu 1601 UV-visible spectrophotometer by layering the mull of the sample to inside of one of the cuvettes while keeping second one layered with Nujol as reference. Thermogravimetric analyses of the complexes were carried out using Perkin-Elmer (Pyris Diamond). Scanning Electron Micrographs (SEM) of polymer-anchored ligands and complexes were recorded on a Leo instrument model 435 VP. Samples were dusted on alumina and coated with a thin film of gold to make the surface conductive, to prevent surface changing and to protect the surface material from thermal damage by the electron beam.

2.2. Preparations

2.2.1. Preparation of 2-(2'-hydroxyphenyl)benzimidazole (Hhpbmz, **I**)

Ligand 2-(2'-hydroxyphenyl)benzimidazole was prepared according to the method reported in the literature [44]. In a typical procedure, equimolar amounts of *o*-phenylenediamine and salicylic acid were mixed with a sufficient quantity of polyphosphoric acid to give a thick paste. The mixture was heated slowly to 250 °C, and the resulting melt was stirred for 4 h. Thereafter, the temperature was lowered to ca. 100 °C and poured with a thin stream into a large volume of rapidly stirred chilled water. The insoluble residue was collected by filtration and washed with a small amount of water. The obtained solid was further mixed with an excess of 10% sodium carbonate solution. The alkaline slurry was filtered after stirring for 1 h, washed thoroughly with water and dried at 60 °C. The crude product was treated with activated charcoal in refluxing alcohol. After filtering and cooling, the pure compound was obtained in 30% yield. mp 242 °C (Lit. 242 °C [44]).

2.2.2. Preparation of polymer-anchored ligand (PS-Hhpbmz, **II**)

Chloromethylated polystyrene (5.5 g) was allowed to swell in DMF (35 ml) for 2 h. A solution of 2-(2'-hydroxyphenyl)benzimidazole (15.30 g, 72.87 mmol) in DMF (40 ml) was added to the above suspension followed by triethylamine (9.0 g) in ethylacetate (40 ml). The reaction mixture was heated at 80 °C for 8 h while stirring mechanically. After cooling to room temperature, the creamish resin was filtered off, washed thoroughly with hot DMF followed by hot methanol and dried in an air oven at ca. 120 °C.

2.2.3. Preparation of PS-[VO(hpbmz)₂] (**1**)

The polymer-anchored ligand (2.0 g) was allowed to swell in DMF (30 ml) for 2 h. A solution of [VO(acac)₂] (5.61 g, 21.2 mmol) in DMF (30 ml) was added to the above suspension and the reaction mixture was heated at 80 °C for 8 h in an oil bath with mechanical stirring. The mixture was cooled to room temperature and dark green beads were filtered off, washed thoroughly with hot DMF followed by methanol and dried in an air oven at ca. 120 °C.

2.2.4. Preparation of PS-[MoO₂(hpbmz)₂] (**2**)

Complex PS-[MoO₂(hpbmz)₂] was prepared following the procedure outlined for **1** using polymer-anchored ligand PS-Hhpbmz and [MoO₂(acac)₂].

2.2.5. Preparation of PS-[Cu(hpbmz)₂] (**3**)

PS-Hhpbmz, (2.0 g) was allowed to swell in DMF (30 ml) for 2 h. A solution of Cu(CH₃COO)₂·H₂O (4.24 g, 21.2 mmol) in DMF (40 ml) was mixed to the above suspension and the reaction mixture was heated at 80 °C for 12 h while stirring mechanically. The mixture was cooled to room temperature and dark blue beads were suction filtered, washed thoroughly with hot DMF followed by hot methanol and dried in an air oven at ca. 120 °C.

2.2.6. Preparation of [VO(hpbmz)₂] (4)

A stirred solution of Hhpbmz (2.52 g, 10 mmol) in dry methanol (50 ml) was treated with [VO(acac)₂] (1.33 g, 5 mmol) dissolved in dry methanol (25 ml) by slow addition and the resulting reaction mixture was stirred for 2 h at room temperature. A green precipitate of [VO(hpbmz)₂] that had separated was filtered off, washed with methanol and dried in vacuo. Yield: 80%.

2.2.7. Preparation of [MoO₂(hpbmz)₂] (5)

Complex [MoO₂(hpbmz)₂] was prepared according to the procedure reported in the literature [45] and dried in vacuo. Yield: 80%.

2.2.8. Preparation of [Cu(hpbmz)₂] (6)

A stirred solution of Hhpbmz (1.26 g, 6 mmol) in methanol (25 ml) was treated with Cu(CH₃COO)₂·H₂O (0.60 g, 3 mmol) dissolved in methanol (30 ml) and the resulting reaction mixture was stirred at room temperature for 2 h. After reducing the solvent volume to ca. 15 ml and keeping at room temperature for over night, a greenish solid precipitated out. This was filtered off, washed with methanol and dried in vacuo. Yield: 78%.

2.3. Catalytic activity studies

Catalytic experiments were carried out in a 50 ml two-necked reaction flask fitted with a septum and water condenser. All catalysts were kept in acetonitrile for at least 2 h for swelling before their use for the catalytic reactions.

2.3.1. Oxidation of styrene

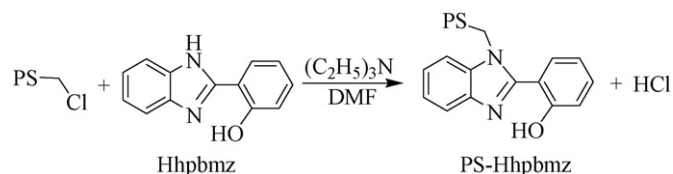
An aqueous 30% H₂O₂ (2.28 g, 20 mmol) and styrene (1.04 g, 10 mmol) were mixed in 20 ml of CH₃CN and the reaction mixture was heated at 80 °C with continuous stirring in an oil bath. An appropriate catalyst (0.025 g) to be tested was added to the reaction mixture and the progress of the reaction was monitored periodically by withdrawing small aliquot and analysing quantitatively by Thermolectron gas chromatograph equipped with HP-1 capillary column (30 m × 0.25 μm × 0.25 mm) and FID detector. The identity of the products was confirmed by GC-MS (Perkin-Elmer, Clarus 500).

2.3.2. Oxidation of ethylbenzene

Ethylbenzene (1.06 g, 10 mmol), 30% aqueous H₂O₂ (3.4 g, 30 mmol) and catalyst (0.030 g) in 20 ml acetonitrile were heated at 80 °C and the reaction was monitored as mentioned above.

2.3.3. Oxidation of methyl phenyl sulfide

Aqueous 30% H₂O₂ (2.28 g, 20 mmol) and catalyst (0.025 g) were added to a solution of methyl phenyl sulfide (1.24 g, 10 mmol) dissolved in acetonitrile (15 ml) and the reaction mixture was stirred at ambient temperature for 2 h. The formation of reaction products was monitored by GC, as mentioned above.



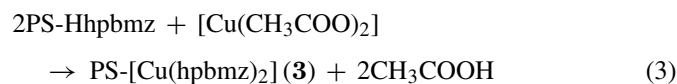
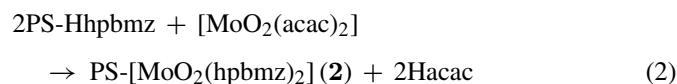
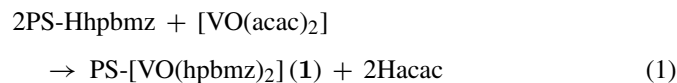
Scheme 2.

3. Results and discussion

3.1. Synthesis and characterisation

Reaction between chloromethylated polystyrene, cross-linked with 5% divinylbenzene, and 2-(2'-hydroxyphenyl)benzimidazole (Hhpbmz, I) in DMF in the presence of triethylamine leads to the formation of polymer-anchored ligand PS-Hhpbmz. During this process –CH₂Cl group of the functionalized polymer reacts with imine nitrogen of the benzimidazole moiety as shown in Scheme 2. Recently, we observed that imine nitrogen of the benzimidazole moiety easily forms covalent bond with chloromethylated polystyrene by above procedure [46]. Miller and Sherrington [47] have shown that 2-(2-pyridyl)imidazole can be covalently bonded to polystyrene through imine nitrogen, by the reaction of ligand and chloromethylated polystyrene in refluxing toluene. Based on the 5.81% of nitrogen observed for PS-Hhpbmz, the loading of anchored ligand was found to be 1.38 mmol g⁻¹.

The polymer-anchored ligand PS-Hhpbmz readily reacts with [VO(acac)₂], [MoO₂(acac)₂] and Cu(CH₃COO)₂ in DMF to give the complexes, PS-[VO(hpbmz)₂] (1), [PS-[MoO₂(hpbmz)₂] (2) and PS-[Cu(hpbmz)₂] (3), respectively. Eqs. (1)–(3) represent the synthetic procedures. A change in the colour of the beads can also be visualized during the reactions:



Neat complexes, [VO(hpbmz)₂] (4), [MoO₂(hpbmz)₂] (5) and [Cu(hpbmz)₂] (6) were also prepared similarly. Physico-chemical data of the isolated complexes are presented in Tables 1 and 2. These data show that metal to ligand loading in polymer complexes is closely to 1:2. Scheme 3 presents the proposed structures of anchored complexes; neat complexes are expected to have similar structure. These structures have been established on the basis of elemental analyses, spectroscopic (IR and electronic) studies, scanning electron micrographs (SEM) and thermo gravimetric patterns (vide infra).

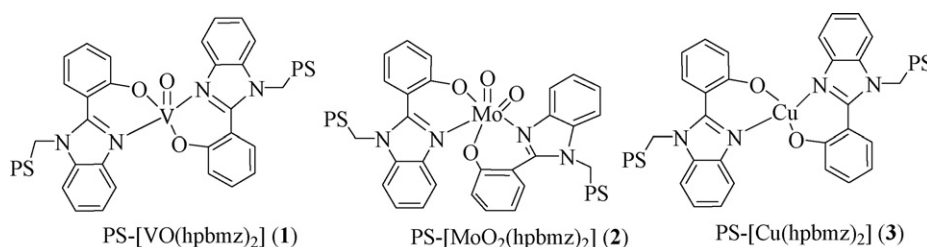
Table 1
Physical and analytical data of neat and polymer-anchored ligands and complexes

Compound	Colour	% Found ^a			
		C	H	N	M
PS-Hhpbmz	Orange	82.94	9.57	5.81	–
PS-[VO(hpbmz) ₂]	Black	66.69	8.73	3.93	3.61
PS-[Cu(hpbmz) ₂]	Black	62.89	7.513	3.81	4.35
PS-[MoO ₂ (hpbmz) ₂]	Black	60.24	6.92	3.45	5.49
Hhpbmz	Brown	73.92 (74.27)	4.83 (4.79)	13.16 (13.32)	–
[VO(hpbmz) ₂]	Green	63.92 (64.34)	3.86 (3.74)	11.22 (11.54)	–
[Cu(hpbmz) ₂]	Brown	64.42 (64.79)	4.00 (3.76)	11.70 (11.62)	–
[MoO ₂ (hpbmz) ₂]	Orange	57.27 (57.15)	3.44 (3.32)	10.02 (10.25)	–

^a Calculated values for neat ligand and complexes are given in parenthesis.

Table 2
Ligand and metal ion loading and ligand to metal ratio data for polymer-anchored complexes

Compound	Ligand loading (mmol equiv. g ⁻¹ of resin)	Metal ion loading (mmol equiv. g ⁻¹ of resin)	Ligand:metal ratio
PS-[VO(hpbmz) ₂]	1.40	0.71	2:1
PS-[Cu(hpbmz) ₂]	1.36	0.69	1.97:1
PS-[MoO ₂ (hpbmz) ₂]	1.23	0.57	2.1:1



Scheme 3.

3.1.1. Thermo gravimetric study

The polymer-anchored complexes are stable up to 150 °C and thereafter they decompose in several small fragments with exothermic weight loss. The weight loss between temperature 150 and 500 °C in complexes **1** and **2** is due to the decomposition of coordinated ligand followed by polystyrene residue. It has not been possible to separate the weight loss due to ligand residue from the weight loss due to polymeric framework because of their overlapping nature. The final residue of 2.3% in **1** and 4.4% in **2** suggests the formation of V₂O₅ and MoO₃. Similar decomposition pattern has also been observed for PS-[Cu(hpbmz)₂] except the complete decomposition at ca. 575 °C. The remaining residue of 6.6% due to CuO formation suggests the presence of copper complex in the polymer matrix.

3.1.2. IR spectral study

A partial list of IR spectral data of polymer-anchored ligand and its complexes along with their neat analogues are listed in Table 3. Ligand 2-(2'-hydroxyphenyl)benzimidazole exhibits the ν(NH) stretching band at 3254(m) cm⁻¹ as a broad band, the hydrogen bonded ν(OH) at 2810(b) and the ν(C=N) at 1632 cm⁻¹ [45]. Disappearance of the ν(NH) band on anchoring with chloromethylated polystyrene suggests the covalent bond formation of ligand through imine nitrogen (cf. Scheme 3). The

band appearing at 2810 cm⁻¹ weakens and a broad band around 3400 appears instead. The ν(C=N) band maintains its original position. A shift of the ν(C=N) (ring) stretching band to lower frequency and absence of the ν(OH) band in all the complexes suggest the coordination of the tertiary nitrogen and phenolic oxygen of the ligand to the metal. The position of the ν(NH) band remains nearly unchanged in neat complexes as compared to Hhpbmz. In addition, vanadium complexes exhibit a strong band at 986 cm⁻¹ (in PS-[VO(hpbmz)₂]) and at 995 cm⁻¹ (in [VO(hpbmz)₂]) due to ν(V=O) stretch while molybdenum complexes exhibit two such bands in the region 880–943 cm⁻¹ due to ν_{sym}(O=Mo=O) and ν_{asym}(O=Mo=O) stretches.

Table 3
IR and electronic spectral data of neat as well as anchored complexes

Complexes	ν(C=N)	ν(M=O)
PS-Hhpbmz	1629	–
PS-[VO(hpbmz) ₂]	1604	986
PS-[MoO ₂ (hpbmz) ₂]	1625	943, 901
PS-[Cu(hpbmz) ₂]	1604	–
[VO(hpbmz) ₂]	1605	995
[MoO ₂ (hpbmz) ₂]	1604	934, 880
[Cu(hpbmz) ₂]	1605	–

Table 4
Electronic spectral data of ligands and complexes

Compound	Solvent	λ_{\max} (nm)
PS-Hhpbmz	Nujol	335, 319, 292, 240, 208
PS-[VO(hpbmz) ₂]	Nujol	339, 322, 295, 234, 218
PS-[MoO ₂ (hpbmz) ₂]	Nujol	337, 305, 234, 210
PS-[Cu(hpbmz) ₂]	Nujol	365, 301, 224
Hhpbmz	Methanol	330, 316, 292, 248, 237, 213
[VO(hpbmz) ₂]	Methanol	602, 536, 362, 330, 318, 292, 248, 240, 214
[MoO ₂ (hpbmz) ₂]	Methanol	362, 330, 318, 292, 248, 240, 214
[Cu(hpbmz) ₂]	Methanol	650, 350, 295, 287, 246, 237, 220

3.1.3. Electronic spectral studies

A list of electronic spectral data of ligands and complexes is presented in Table 4. The neat ligand exhibits five bands at 330, 316, 292, 248, 237 and 213 nm in the UV region. The first two bands are characteristic of the presence of benzimidazole group, 292 nm band due to $n \rightarrow \pi^*$ while next two bands due to split $\pi \rightarrow \pi^*$ and 213 nm band due to $\phi \rightarrow \phi^*$ transitions. Neat complexes, PS-[VO(hpbmz)₂] and PS-[MoO₂(hpbmz)₂] exhibit characteristic bands due to benzimidazole group as well as other ligand bands at nearly the same positions. A considerable shift of the characteristic benzimidazole bands towards higher energy has been noticed in [Cu(hpbmz)₂] and because of this the band due to $n \rightarrow \pi^*$ transition could not be located. A broad charge transfer band at ca. 360 nm has also been observed in all complexes. In addition, [VO(hpbmz)₂] exhibits two weak bands at 536 and 602 nm while [Cu(hpbmz)₂] exhibits a broad band at ca. 650 nm (not shown in the figure) due to d–d transition(s). Such d–d band in polymer-anchored complexes, PS-[VO(hpbmz)₂] and PS-[Cu(hpbmz)₂] could not be located while other UV- visible bands as shown in Fig. 1 have been observed with weak inten-

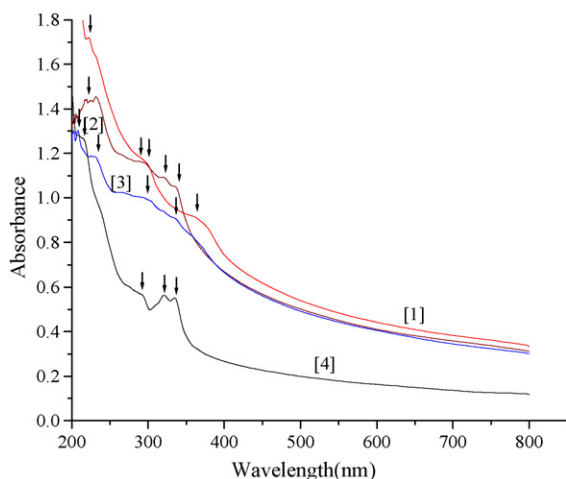
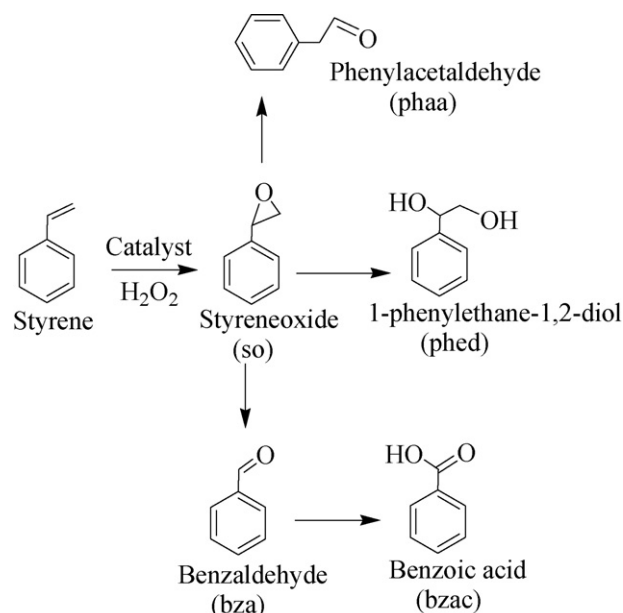


Fig. 1. Electronic spectra of PS-[Cu(hpbmz)₂] (1), PS-[MoO₂(hpbmz)₂] (2), PS-[VO(hpbmz)₂] (3) and PS-Hhpbmz (4) recorded in Nujol.



Scheme 4.

sity. All these indicate the presence of complexes in the polymer matrix but with weak loading.

3.1.4. Scanning electron micrograph study

Scanning electron micrographs (SEM) of single bead of pure chloromethylated polystyrene, polymer-anchored ligand PS-Hhpbmz and its complexes [VO(hpbmz)₂], [MoO₂(hpbmz)₂] and [Cu(hpbmz)₂] were recorded to observe the morphological changes. Some of these images are given in Fig. S-1 in supplementary material section. As expected pure polystyrene bead has smooth and flat surface while anchored ligand and complexes show slight roughening of the top layer. This roughening is relatively more in complexes. This is possibly due to interaction of the metal ions with anchored ligand that resulted in the formation of complex with fixed geometry. Accurate information on the morphological changes in terms of exact orientation of ligand coordinated to the metal ions has not been possible due to poor loading of the metal complexes.

3.2. Catalytic activity

3.2.1. Oxidation of styrene

Oxidation of styrene, catalysed by PS-[VO(hpbmz)₂], PS-[MoO₂(hpbmz)₂] and PS-[Cu(hpbmz)₂], using H₂O₂ as oxidant gave five oxidation products namely, styrene oxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid and phenylacetaldehyde (Scheme 4). Hulea et al. [48] have reported some of these product during the oxidation of styrene using TS-1 and MCM-41. At least five oxidation products have recently been obtained using polymer-anchored catalysts PS-[VO(sal-ohya)-DMF] [49] and PS-K[VO(O₂)(L)] [L = 2-(2-pyridyl)benzimidazole and 2-(3-pyridyl)benzimidazole] [46]. Amongst the polymer-anchored complexes, PS-[Cu(hpbmz)₂] was taken as a representative and four different parameters, viz. amount of oxidant (moles of H₂O₂ per mole of styrene), amount

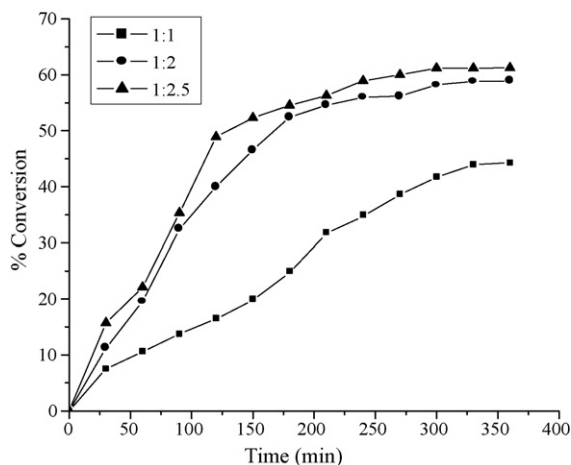


Fig. 2. Effect of amount of H_2O_2 on the oxidation of styrene. Reaction conditions: styrene (1.04 g, 10 mmol), PS-[Cu(hpbmz)₂] (0.025 g), CH_3CN (20 ml) and temperature (80 °C).

of catalyst and solvent, and temperature of the reaction mixture were varied to optimise the reaction conditions for the maximum oxidation of styrene.

For the styrene:aqueous 30% H_2O_2 molar ratios of 1:1, 1:2 and 1:2.5, the mixture of styrene (1.04 g, 10 mmol) and catalyst (0.025 g) were taken in 20 ml of CH_3CN and the reaction was carried out at 80 °C. As illustrated in Fig. 2, the percent conversion of styrene improved from 44.3 to 61.2% on increasing the styrene:oxidant ratio from 1:1 to 1:2. Further increasing this ratio to 1:2.5 hardly affected the conversion, suggesting that 1:2 (styrene: H_2O_2) ratio is sufficient enough to perform the reaction with good conversion. Similarly, for three different amounts viz. 0.015, 0.025 and 0.035 g of catalyst and at the styrene: H_2O_2 ratio of 1:2 under above reaction conditions, 0.015 g catalyst gave only 48.1% conversion whereas 0.025 and 0.035 g catalyst have shown a maximum conversion of 58.8 and 54.5%, respectively (Fig. 3). The limitation in conversion of styrene with higher amount of catalyst is not due to the interaction of benzoic

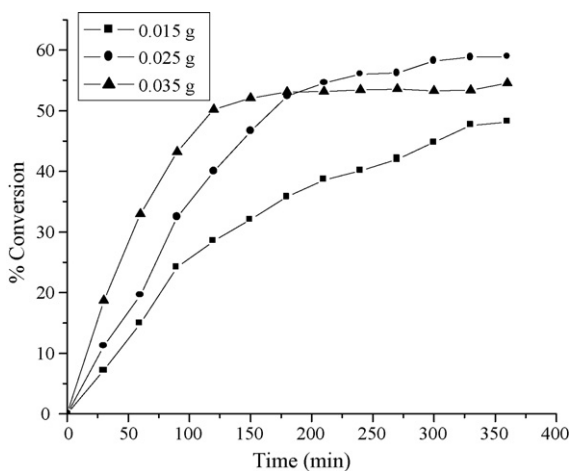


Fig. 3. Effect of amount of catalyst on the oxidation of styrene. Reaction conditions: styrene (1.04 g, 10 mmol), H_2O_2 (1.586 g, 20 mmol), CH_3CN (20 ml) and temperature (80 °C).

acid formed in the reaction mixture as titration of neat complex [Cu(hpbmz)₂] with benzoic acid does not alter any peaks position of its electronic spectrum in methanol. Such phenomenon has also previously been observed and has been interpreted in terms of thermodynamic and mass transfer limitations at higher reaction rates, etc. [50].

The effect of temperature on the performance of catalyst was studied at three different temperatures, viz. 60, 70 and 80 °C at the fixed amount of styrene (1.04 g, 10 mmol), H_2O_2 (2.28 g, 20 mmol) and PS-[Cu(hpbmz)₂] (0.025 g) in 20 ml CH_3CN . A maximum of 58.9% conversion was achieved on carrying out the reaction at 80 °C. Other reaction temperature gave lower conversion. It was also observed that the time required to achieve the maximum conversion was relatively less at 80 °C. The effect of the solvent amount on the performance of catalyst was also studied under above optimised conditions and as shown in Fig. S-2 of the supplementary material section, running the reaction in 20 ml and 25 ml of acetonitrile gave a comparable result of 61.0 and 58.8% conversion. Running the reaction in 15 ml acetonitrile has shown only 43.1% conversion. Thus, at least 20 ml acetonitrile is an optimum amount to obtain better conversion.

Under the above optimised conditions i.e. styrene (1.26 g, 10 mmol), 30% H_2O_2 (2.28 g, 20 mmol), catalyst (0.025 g), CH_3CN (20 ml) and temperature (80 °C), other catalysts, e.g. PS-[VO(hpbmz)₂] and PS-[MoO₂(hpbmz)₂] were also tested and the obtained results are shown in Fig. 4. Table 5 provides conversion details along with the selectivity of the various products after 6 h of reaction time. It is clear that PS-[VO(hpbmz)₂] exhibits better catalytic conversion (69.6%) than PS-[Cu(hpbmz)₂] (58.8%). The PS-[MoO₂(hpbmz)₂], on the other hand, exhibits only 23.4% conversion. Though, all the complexes reacts with H_2O_2 to generate peroxo species in solution (vide infra), the poor catalytic activity of PS-[MoO₂(hpbmz)₂] may be due to the difficulty in transferring oxygen from the intermediate peroxo species to the substrate. Such results have also been observed earlier with other polymer-anchored heterogeneous catalysts [46].

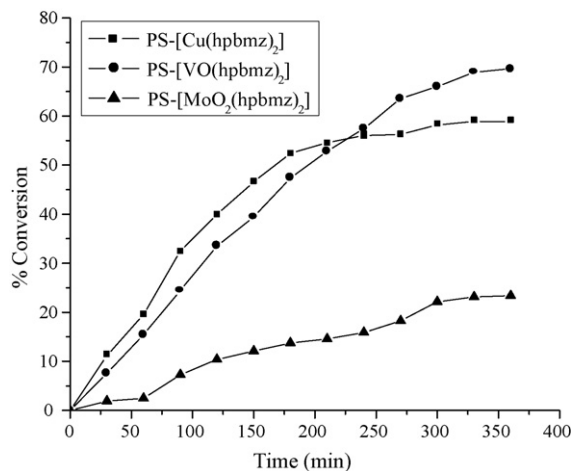


Fig. 4. Catalytic comparison of catalysts for the oxidation of styrene. Reaction conditions: styrene (1.04 g, 10 mmol), catalyst (0.025 g), H_2O_2 (1.586 g, 20 mmol), CH_3CN (20 ml) and temperature (80 °C).

Table 5

Percent conversion of styrene along with turn over frequency and selectivity of different reaction products

Catalyst	% Conversion	TOF (h ⁻¹)	% Selectivity ^a				
			so	phaa	bza	bzac	phed
PS-[Cu(hpbmz) ₂]	58.9	57.3	1.85	12.70	57.55	15.60	12.30
PS-[VO(hpbmz) ₂]	70.8	66.7	5.17	1.13	72.23	5.78	15.69
PS-[MoO ₂ (hpbmz) ₂]	23.4	27.1	3.07	10.26	81.59	3.81	1.26
[Cu(hpbmz) ₂]	26.3	4.0	0.72	6.47	79.27	4.66	9.51
[VO(hpbmz) ₂]	51.9	8.1	2.96	1.41	82.39	2.97	10.08
[MoO ₂ (hpbmz) ₂]	13.3	2.6	0.95	9.85	86.12	0.39	2.68

^a so: styreneepoxide; phaa: phenylacetaldehyde; bza: benzaldehyde; bzac: benzoic acid; phed: 1-phenylethane-1,2-diol.

The catalytic activity of neat complexes, [VO(hpbmz)₂] (**4**), [MoO₂(hpbmz)₂] (**5**) and [Cu(hpbmz)₂] (**6**) have also been studied. Table 5 provides selectivity details of various products obtained after 6 h of reaction time. Using same molar concentration of neat complexes i.e. **4** (0.0055 g), **5** (0.0081 g) and **6** (0.0070 g), under the above optimised conditions the obtained conversion percentage of styrene varied in the order: **4** (51.9%) > **6** (26.3 %) > **5** (13.3%). Though, the conversion is relatively low with all neat complexes, the order of reaction products is similar to the one observed for polymer-anchored complexes. The formation of benzaldehyde in highest yield with all catalysts is understandable because the styrene oxide formed in the first step may convert into benzaldehyde by a nucleophilic attack of H₂O₂ to styrene oxide followed by a cleavage of the intermediate hydroperoxystyrene. Benzaldehyde formation may also be facilitated by direct oxidative cleavage of the styrene side chain double bond via radical mechanism [48]. The formation of benzoic acid through benzaldehyde, though slow, is also understandable in all reactions. Similarly, the formation of phenylacetaldehyde, a product formed by isomerisation of styrene oxide is less in all cases. Water present in H₂O₂ is probably responsible for hydrolysis of styrene oxide to 1-phenylethane-1,2-diol to some extent.

3.2.2. Oxidation of ethylbenzene

Oxidation of ethylbenzene has mostly been carried out using molecular oxygen as oxidant and there are only limited reports where TBHP/H₂O₂ has been used as oxidant [24–35]. With mild oxidant usually acetophenone is obtained as major products while strong oxidant gives several oxidized products. Acetophenone, an important oxidized product, has been used as an intermediate in pharmaceuticals, resins, alcohols, esters, aldehydes, and tear gas. We have also tested the catalytic potential of the polymer-anchored complexes for the oxidation of ethylbenzene using H₂O₂ as oxidant. The oxidation of ethylbenzene gave reaction products, benzaldehyde, phenyl acetic acid, styrene

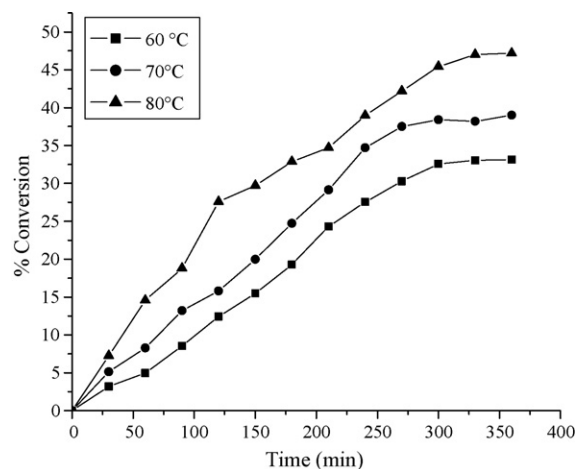
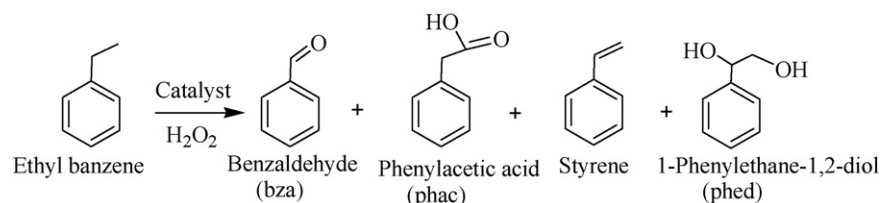


Fig. 5. Effect of temperature on the oxidation of ethylbenzene. Reaction conditions: ethylbenzene (1.04 g, 10 mmol), PS-[Cu(hpbmz)₂] (0.025 g), H₂O₂ (1.586 g, 20 mmol) and CH₃CN (20 ml).

and 1-phenylethane-1,2-diol as shown in Scheme 5 have been obtained.

Reaction condition has been optimised for the maximum conversion by varying the amount of oxidant (moles of H₂O₂ per mol of ethylbenzene) amount of catalyst and temperature of the reaction considering PS-[Cu(hpbmz)₂] as a representative catalyst.

Effect of temperature on the oxidation of ethylbenzene as a function of time for the fixed amount of ethylbenzene (1.06 g, 10 mmol), 30% H₂O₂ (3.4 g, 30 mmol) and catalyst (0.025 g) in 20 ml CH₃CN has been plotted in Fig. 5. It is clear from the figure that the performance of catalyst at 80 °C is much better as compared to lower temperatures. Fig. 6 records the results obtained by varying the H₂O₂:ethylbenzene ratios. Only 18.3% conversion has been achieved at the H₂O₂:ethylbenzene molar ratio of 1:1 in CH₃CN (20 ml) at 80 °C after 6 h of reaction time under the above conditions. Increasing this ratio to 2:1 enhanced



Scheme 5.

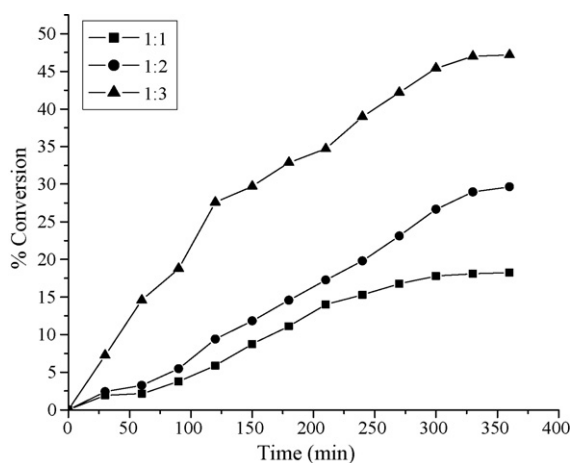


Fig. 6. Effect of amount oxidant on the oxidation of ethylbenzene. Reaction conditions: ethylbenzene (1.06 g, 10 mmol), PS-[Cu(hpbmz)₂] (0.025 g), temperature (80 °C) and CH₃CN (20 ml).

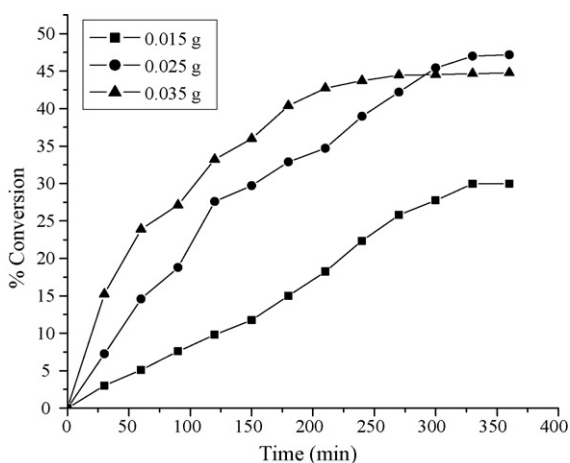


Fig. 7. Effect of amount of PS-[Cu(hpbmz)₂] on the oxidation of ethylbenzene. Reaction conditions: ethylbenzene (1.06 g, 10 mmol), H₂O₂ (3.4 g, 30 mmol), temperature (80 °C) and CH₃CN (20 ml).

the conversion to 29.7%, which further went up to 47.1% at 3:1 ratio. Further increment of H₂O₂ concentration showed poor result possibly due to the presence of excess water in the reaction mixture.

The effect of amount of catalyst on the oxidation of ethylbenzene is illustrated in Fig. 7. It is clear from the plot that amongst three different amounts viz. 0.015, 0.025 and 0.035 g of catalyst

at the H₂O₂:ethylbenzene ratio of 3:1 under the above reaction condition, 0.025 g of catalyst has shown maximum conversion of 47.2% while 0.015 g and 0.035 g catalyst gave 30.0 and 44.8% conversion, respectively. Thus, the optimised amount for the best performance of the catalyst is 0.025 g.

All these studies concluded the following best-suited reaction conditions for the maximum oxidation ethylbenzene:ethylbenzene (1.06 g, 10 mmol), aqueous 30% H₂O₂, (3.42 g, 30 mmol), catalyst (0.025 g), CH₃CN (20 ml) and temperature (80 °C). Under these conditions, PS-[Cu(hpbmz)₂] gave a maximum conversion of 47.2% after 6 h of reaction time. A moderate conversion of 31.2% has been obtained with PS-[VO(hpbmz)₂] while only 12.5% conversion could be achieved with PS-[MoO₂(hpbmz)₂]. However, the selectivity of the products was found to be independent of these catalysts and followed the order: benzaldehyde > phenyl acetic acid > styrene > 1-phenylethane-1,2-diol. A very small amount of unidentified product has also been noticed (see Table 6) and this is possibly due to the other oxidized products. No significant improvement in the oxidation of ethylbenzene was observed beyond 6 h of reaction time.

The corresponding neat complexes, [Cu(hpbmz)₂], [VO(hpbmz)₂] and [MoO₂(hpbmz)₂] showed relatively poor conversion (Table 6), though, one should expect the higher conversion with homogeneous catalyst. This is possibly due to the insolubility of the catalysts in acetonitrile that reduces their dispersion in solvent and thus availability of low surface area to interact with the oxidant. Better turn over frequency and higher catalytic potential of polymer-anchored catalysts along with other properties as stated in the introduction make them better catalyst over their neat ones.

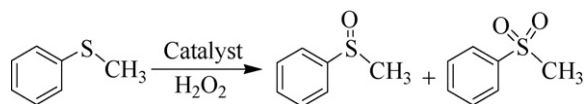
3.2.3. Oxidation of methyl phenyl sulfide

Vanadium complexes are known to catalyse the oxidation of organic sulfides (thioethers) by H₂O₂ to sulfoxides and molybdenum complexes behave similarly to some extent (see introduction). The sulfur atom in methyl phenyl sulfide is electron rich species and facilitates the electrophilic oxidation to give sulfoxide and further to sulfones. We have also tested the oxidation of methyl phenyl sulfide, with these catalysts. The oxidation of methyl phenyl sulfide catalysed by these polymer-anchored catalysts gave a mixture of methyl phenyl sulfoxide and methyl phenyl sulfone in acetonitrile at ambient temperature as shown in Scheme 6.

Table 6
Percent conversion of ethylbenzene along with turn over frequency and selectivity of different reaction products

Catalyst	% Conversion	TOF (h ⁻¹)	% Selectivity ^a				
			phac	bza	Styrene	phed	Others
PS-[Cu(hpbmz) ₂]	47.2	45.4	7.67	63.29	2.84	17.83	8.34
PS-[VO(hpbmz) ₂]	31.2	29.4	7.60	72.22	2.23	16.42	1.53
PS-[MoO ₂ (hpbmz) ₂]	12.5	14.6	8.54	74.31	3.42	12.84	0.89
[Cu(hpbmz) ₂]	18.9	2.9	8.61	74.54	3.23	12.95	0.87
[VO(hpbmz) ₂]	17.6	2.7	8.50	76.06	3.01	12.33	0.48
[MoO ₂ (hpbmz) ₂]	7.6	1.5	8.02	75.46	3.54	12.73	0.61

^a phac: phenylacetic acid; bza: benzoic acid; phed: 1-phenylethane-1,2-diol.



Scheme 6.

This conversion increases on increasing the amount of oxidant as demonstrated by considering the catalyst PS-[VO(hpbmz)₂]. As expected, reduction in the yield of sulfoxide while increment in the yield of sulfone on increasing the oxidant has been observed; see Table S-1 of the supplementary material section.

In order to see the effect of catalyst amount on the sulfoxidation, we used 0.015, 0.025 and 0.035 g of PS-[VO(hpbmz)₂] for 30% H₂O₂ (2.8 g, 20 mmol) and methyl phenyl sulfide (1.24 g, 10 mmol) and the reaction was performed at room temperature in 15 ml of acetonitrile. The plot presented in Fig. 8 shows that 0.025 g and 0.035 g catalyst gave nearly same percent conversion while 0.015 g catalyst showed a maximum of 62% conversion. Thus, under the best suited conditions i.e. catalyst (0.025 g), 30% H₂O₂ (2.28 g, 20 mmol), methyl phenyl sulfide (1.24 g, 10 mmol) and CH₃CN (15 ml), a maximum of 76.5% conversion with 77.4% selectivity towards sulfoxide and 22.6% towards sulfone has been achieved.

Under these conditions, PS-[MoO₂(hpbmz)₂] has shown comparable (75.1%) catalytic activity while only 44.8% conversion has been achieved with PS-[Cu(hpbmz)₂]. Irrespective of their catalytic performances, the selectivity for the formation of sulfoxide is almost similar for all these catalysts (Table 7).

Other polymer-anchored metal complexes as well as neat complexes were also tested for the oxidation of methyl phenyl sulfide. Details of the conversion and selectivity of the products are presented in Table 7. A blank reaction under the similar conditions (10 mmol methyl phenyl sulfoxide, 20 mmol H₂O₂ in 15 ml CH₃CN) resulted in 35.2% conversion of methyl phenyl sulfide with 68.3% selectivity towards sulfoxide and 31.7% towards sulfones. Thus, these catalysts not only enhance the conversion of methyl phenyl sulfide but also enhance the selectivity toward the formation of sulfoxide.

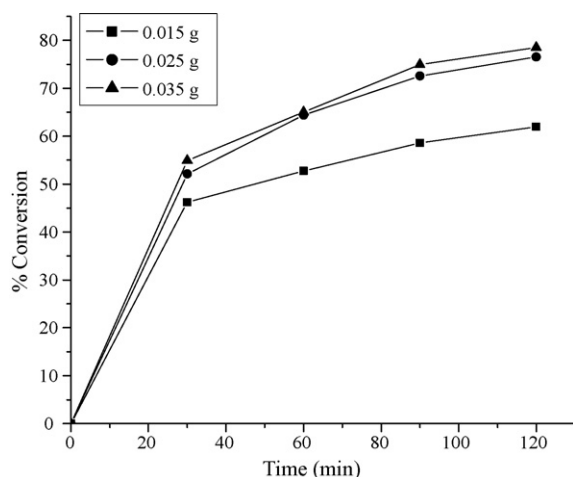


Fig. 8. Effect of amount of PS-[VO(hpbmz)₂] on the oxidation of methyl phenyl sulfide.

Table 7

Percent conversion of methyl phenyl sulfide along with turn over frequency and selectivity of the reaction products

Complexes	% Conversion	TOF (h ⁻¹)	% Selectivity	
			Sulfoxide	Sulfone
Ps-[Cu(hpbmz) ₂]	44.8	43.6	73.4	26.6
Ps-[VO(hpbmz) ₂]	76.5	72.1	77.4	22.6
Ps-[MoO ₂ (hpbmz) ₂]	75.1	87.5	75.9	24.1
[Cu(hpbmz) ₂]	39.7	6.03	72.5	27.9
[VO(hpbmz) ₂]	54.8	8.53	67.0	33.0
[MoO ₂ (hpbmz) ₂]	55.2	10.9	72.83	27.26

3.3. Recycle ability and heterogeneity of the reaction

To ensure the recycle ability of the polymer-anchored catalysts, we separated the catalysts from the reaction mixtures and after washing with acetonitrile they were further applied for catalytic reactions under similar conditions in all three cases. No appreciable loss in the catalytic activity suggested the recycle ability of the catalysts. The filtrate collected was placed further for reaction at optimised conditions for 3 h. The gas chromatographic analysis of the reaction mixture showed no further increment in the conversion. This confirms that the reactions did not proceed on the removal of the solid catalysts and hence the reactions were heterogeneous in nature. In addition to this, the filtrates were tested by ICP-MS/AAS for the leaching of metal ions and it showed the absence of metal ions in the filtrate.

3.4. Possible reaction pathways of the catalysts

In order to establish the reaction pathway, the methanolic solution of [Cu(hpbmz)₂] was treated with H₂O₂ diluted in methanol and spectral changes, monitored by electronic absorption spectroscopy, are presented in Fig. 9. Thus, the drop wise addition of dilute methanolic solution of 30% H₂O₂ resulted in the increment of 350, 295, 287 and 246 nm bands. Similarly, the 237 nm band gains marginal intensity while the band appearing

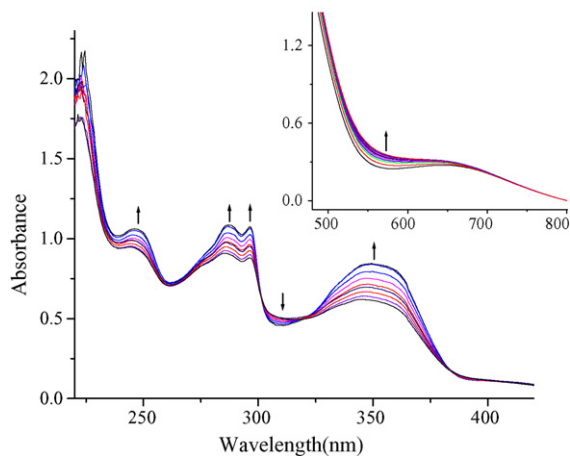


Fig. 9. Titration of [Cu(hpbmz)₂] with H₂O₂. Spectra were recorded after the successive addition of one drop portions of H₂O₂ dissolved in methanol to 10 ml of ca. 10⁻⁴ M solution of [Cu(hpbmz)₂].

at 220 nm gains intensity rapidly. The presence of two isosbestic points at 320 and 301 nm suggests the transformation of Cu(II) complex to peroxy species.

At least three types of intermediates having copper-oxygen interaction viz. side-on $\text{Cu}^{\text{III}}-(\mu-\eta^2\text{-peroxy})-\text{Cu}^{\text{III}}$, bis(μ -oxo- Cu^{III}) and $\text{Cu}^{\text{III}}\text{-O-O-H}$ (copper-hydroperoxide) have been reported in the literature during catalytic action [51,52]. The facile formation of $[(\text{HOO})\text{-Cu}(\text{hpbmz})_2]$ intermediate is expected in $\text{PS-}[\text{Cu}(\text{hpbmz})_2]$ as metal centers in the polymer-supported complexes are well separated. This intermediate transfers the coordinated oxygen atoms to the substrates to give the products. Thus, the catalytic performance of supported catalyst could be attributed to the formation of facile and reversible intermediate hydroperoxide species. A slight broadening in d–d transition band of 650 nm along with marginal increment in intensity without isosbestic point in neat complex hints the merging of the d–d band with additional charge transfer band possibly due to Cu-hydroperoxide complex formation; a characteristic charge transfer band due to Cu-hydroperoxide is known to appear around 600 nm [53]. Based on observed reaction products, the mode of action of Cu-hydroperoxide in the oxidation seems to be similar in neat and supported complexes.

Similar titrations for complexes, $[\text{VO}(\text{hpbmz})_2]$ and $[\text{MoO}_2(\text{hpbmz})_2]$ have also been carried out. In $[\text{VO}(\text{hpbmz})_2]$ (Fig. 10), the intensity of 362 nm band was slowly diminished. At the same time, the bands appearing at 330 and 318 nm gained intensity without any change in their positions. The band position as well as intensity of the 292 nm band remained constant while the intensity of the 240 and 248 nm bands partially decreased. These spectral changes indicate the interaction of vanadium(IV) center with H_2O_2 . Since oxovanadium(IV) complexes are known to form oxoperoxovanadium(V) species [54], we also suggest the in situ formation of oxoperovanadium(V) complex that transfer oxygen to the substrate during oxidation. This is supported by the disappearance of d-d bands present in $[\text{VO}(\text{hpbmz})_2]$ at 536 and 602 nm and the appearance of isosbestic points at 508 and 452 nm. Dioxomolybdenum(VI) complex exhibits exactly similar spectral features on treatment

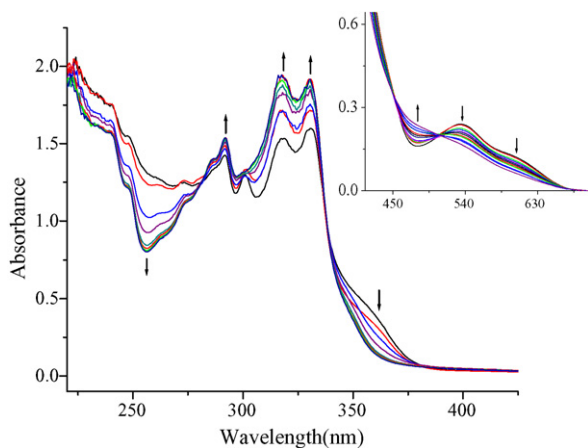


Fig. 10. Titration of $[\text{VO}(\text{hpbmz})_2]$ with H_2O_2 . Spectra were recorded after the successive addition of one drop portions of H_2O_2 dissolved in methanol to 10 ml of ca. 10^{-4} M solution of $[\text{VO}(\text{hpbmz})_2]$.

with H_2O_2 ; see Fig. S-3 of the supplementary material section, and is due to the formation of oxoperoxomolybdenum(VI) species. However, the expected ligand to metal charge transfer band could not be observed at this concentration.

4. Conclusions

Polymer-anchored complexes, $\text{PS-}[\text{VO}(\text{hpbmz})_2]$, $\text{PS-}[\text{Cu}(\text{hpbmz})_2]$ and $\text{PS-}[\text{MoO}_2(\text{hpbmz})_2]$ ($\text{Hhpbmz} = 2\text{-}(2'\text{-hydroxyphenyl})\text{benzimidazole}$) having potential catalytic activities for the oxidation of styrene, ethylbenzene and methyl phenyl sulfide have been prepared and characterised. Under the optimised conditions, oxidation of styrene gave at least five reaction products namely, styrene oxide, benzaldehyde, 1-phenylethane-1,2-diol, benzoic acid, and phenyl acetaldehyde, and the percentage conversion of styrene varied in the order: $\text{PS-}[\text{VO}(\text{hpbmz})_2]$ (69.9%) > $\text{PS-}[\text{Cu}(\text{hpbmz})_2]$ (58.8%) > $\text{PS-}[\text{MoO}_2(\text{hpbmz})_2]$ (23.4%). The oxidation of ethylbenzene catalysed by $\text{PS-}[\text{Cu}(\text{hpbmz})_2]$ gave a maximum conversion of 47.2% after 6 h of reaction time. Only moderate conversion of 31.2% by $\text{PS-}[\text{VO}(\text{hpbmz})_2]$ and 12.5% by $\text{PS-}[\text{MoO}_2(\text{hpbmz})_2]$ has been achieved. The selectivity of the obtained products follow the order: benzoic acid > 1-phenylethane-1,2-diol > phenylacetic acid > styrene. Catalyst $\text{PS-}[\text{VO}(\text{hpbmz})_2]$ has also shown good catalytic activity towards the oxidation of methyl phenyl sulfide and gave a maximum of 76.5% conversion to the corresponding sulfoxide and sulfone. Under the same conditions, $\text{PS-}[\text{MoO}_2(\text{hpbmz})_2]$ has shown comparable (75.1%) catalytic activity while only 44.8% conversion has been achieved with $\text{PS-}[\text{Cu}(\text{hpbmz})_2]$. Irrespective of their catalytic performances, the selectivity for the formation of sulfoxide is almost similar (ca. 75%) for all these catalysts. All these catalysts are recyclable and heterogeneous in nature.

Acknowledgements

Authors are thankful to Council of Scientific and Industrial research, New Delhi for financial support. Chloromethylated polystyrene generously given by Thermax Ltd., Pune, India is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2007.03.074.

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