Oxidation of phenol and hydroquinone catalysed by copper(II) and oxovanadium(IV) complexes of N,N'-bis(salicyledene)diethylenetriamine (H₂saldien) covalently bonded to chloromethylated polystyrene

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Abstract

Reaction between N,N'-bis(salicyledene)diethylenetriamine (H₂saldien) covalently bonded to chloromethylated polystyrene cross linked with 5% divinylbenzene (abbreviated as PS-H₂saldien, **I**) and aqueous potassium vanadate at ca. pH 6.5 results in the formation of polymer-anchored complex PS-[VO(saldien)] (**1**). Cupric acetate on reaction with **I** in methanol gives PS-[Cu(saldien)] (**2**). Formations of these complexes were confirmed by IR and electronic spectroscopic techniques, elemental and thermo gravimetric analyses and scanning electron micrographs. Catalytic potential of these complexes have been tested for the oxidation of phenol and hydroquinone using 30% H_2O_2 as an oxidant. Various reaction parameters such as substrate to oxidant ratio, concentration of catalysts and solvent of the reaction medium have been optimised to get maximum oxidation of phenol to p-benzoquinone selectively. Under optimised conditions, i.e. phenol (1.88 g, 20 mmol), H_2O_2 (4.56 g, 40 mmol), PS-[Cu(saldien)] (30 mg), temperature (70 °C) and water (10 ml), the phenol conversion was found to be 22.2% and percentage yield of the main products p-benzoquinone and catechol are 14.4% and 7.8%, respectively. PS-[VO(saldien)] exhibits only 3% conversion in water with 100% selectivity towards benzoquinone. Both the catalysts become more selective towards catechol formation along with higher conversion in acetonitrile. The selectivity of p-benzoquinone was also found to be dependent on volume and nature of solvent, and temperature. Hydroquinone oxidation was also found to be pH dependent; carbonate buffer gives quantitative conversion within 30 min at 1:6 substrate to oxidant ratio.
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1. Introduction

Quinones, the important constituent of natural products like co-enzyme and vitamins, are of immense biological importance. They play vital role as electron acceptors in the electron transport system of photosynthesis I and II (Vitamin K1 in phylloquinone) and respiratory element of biosystem. In addition, they exhibit miscellaneous industrial applications as fine chemicals and have been used as polymerizable inhibitor, antioxidant and medicines and as dienophiles in the organic synthesis [1,2]. A general method for the preparation of quinones is the oxidation of phenol and its derivatives [3]. Number of oxidants, e.g.,

mineral acids [4], Fermy's salt [5], lead tetraacetate [6], cerium ammonium nitrate [7], and other transition metal ions [8] have been employed but most of these suffer from the drawback like, homogenous reaction conditions and generation of toxic side wastes. Moreover, all these systems have shown poor para/ortho selectivity. These demanded the development of new catalytic protocols that fulfill the demands for the green chemistry and also provide better selectivity in terms of para to ortho ratio. Several heterogeneous catalytic methods have been developed for the oxidation of phenol that showed significant advantages over their homogeneous counterpart like, easy separation from reaction mixture, thermal stability and recyclability. Several research groups have carried out phenol oxidation using various types of catalysts and reported a wide range of product selectivity [9–22]. Molecular sieve based catalysts, TS-1 and TS-2 have been proved to be the promising catalysts for the hydroxylation

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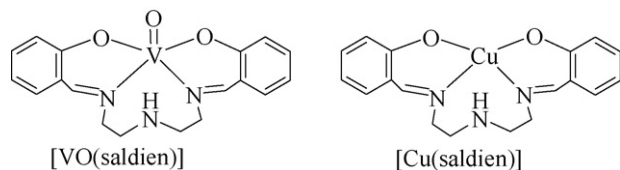
Scheme 1.

of phenol [19–22]; TS-1 catalysts has been commercialised for the oxidation of phenol by Enichem [21]. Attempts have also been made to improve benzoquinone selectivity from phenol oxidation [23–27].

Oxidation of hydroquinone to benzoquinone is also a very important physiological reaction and copper metal is found to be the most efficient catalysts for this reaction. Effort has also been made to study the hydroquinone kinetics in the presence of 30% H_2O_2 as an oxidant [28].

Catalytic potential of [Cu(saldien)] and [VO(saldien)] (H_2 saldien = N,N'-bis(salicyledene)diethylenetriamine) (Scheme 1) has recently been investigated. For example, oxidation of phenol catalysed by [VO(saldien)] [29] and [Cu(saldien)] [30] encapsulated in zeolite-Y has been reported to give catechol and hydroquinone in acetonitrile, where selectivity of catechol was as high as ca. 90% with copper catalyst. Catalytic potential of [VO(saldien)] covalently bonded to functionalized SBA-15 for the oxyfunctionalization of limonene, using urea hydrogenperoxide as an oxidant has been explored by Joseph and Halligudi [31]. We were interested in modifying the catalyst support and reaction conditions to alter the selectivity of catalysts [VO(saldien)] and [Cu(saldien)] towards the formation of *p*-benzoquinone on the oxidation of phenol. In the present investigation, we have, therefore, immobilized these catalysts through covalent bonding to chloromethylated polystyrene and optimised the reaction conditions to improve the selectivity towards the *p*-benzoquinone formation upon the oxidation of phenol. Oxidation of hydroquinone using these catalysts has also been carried out. Amongst heterogeneous catalytic systems, the immobilization of homogenous catalysts onto polymer is also a topic of wide interest [32].

2. Experimental

2.1. Materials

Chloromethylated polystyrene (18.9% Cl i.e. 5.3 mmol Cl/g of resin and 5% cross-linked with divinylbenzene) was obtained as gift from Thermax Limited, Pune, India. Analytical reagent grade cupric acetate monohydrate and phenol were purchased from E. Merck, India. Hydroquinone and DMF were the products of Ranbaxy fine chemicals, India. Vanadium pentaoxide was procured from S.D. finechemicals, India and 30% H_2O_2 was procured from Thomas Baker, India. N,N'-Bis(salicyliden)diethylenetriamine [29,30] and [VO(acac)$_2$] [33] were prepared according to the methods reported in the literature.

2.2. Physical methods and analysis

Elemental analyses of the ligands and complexes were obtained by an Elementary model Vario-EL-III. IR spectra were recorded as KBr pellet on a Nicolet NEXUS Aligent 1100 series FT-IR spectrometer after grinding the sample with KBr. UV–vis spectra of the anchored ligand and complexes were recorded in a nujol on a Shimadzu 1601 UV–vis spectrophotometer by layering the mull of the sample to inside of one of the cuvettes while keeping the other one layered with nujol as reference. Spectra of neat complexes were recorded in methanol. Copper and vanadium analyses of the anchored complexes were obtained by atomic absorption spectrometer (AAS-Hitachi Model Z-8000) after decomposing the complexes with conc. HNO_3 and diluting the filtrate with distilled water (for copper) or with very dilute aqueous KOH solution (in case of vanadium) to specific volume. Scanning electron micrographs (SEM) of the polymer-anchored ligand and complexes were recorded on a Leo instrument model 435 VP after coating the samples with thin film of gold to prevent surface changing and to protect the surface material from thermal damages by the electron beam. Thermogravimetric analysis of the complexes was carried out under oxygen atmosphere using TG Stanton Redcroft STA 780.

2.3. Synthesis

2.3.1. Polymer-anchored N,N'-bis(salicylidene)-diethylenetriamine (PS-H₂saldien, I)

Chloromethylated polystyrene beads (8.0 g, 42.8 mmol equiv. Cl) were allowed to swell in 40 ml of DMF for 2 h at room temperature. A DMF solution (30 ml) of H_2saldien (40.0 g, 128 mmol) was added to the above suspension followed by triethylamine (12.0 g, 118 mmol) in ethylacetate (60 ml); the Cl:ligand ratio was approximated to be 1:3. The obtained reaction mixture was heated at ca. 80 °C in an oil bath while continuous mechanical stirring for ca. 24 h. After cooling to room temperature the reddish-yellow resin beads were filtered off, washed with hot DMF followed by hot ethanol and dried in an air oven at ca. 120 °C. Obs. for (PS-H₂saldien): C, 67.50%; H, 7.19%; N, 5.92%.

2.3.2. PS-[VO(saldien)] (1)

Polymer-anchored ligand, PS-H₂saldien (3.5 g, 4.93 mmol equiv. of nitrogen) was allowed to swell in water for 4 h prior to the reaction. In a separate flask vanadium(V) oxide (3.27 g, 18 mmol) was dissolved in aqueous KOH (1.5 g, 27 mmol in 50 ml) and stirred for 2 h with occasional heating at ca. 50 °C. The potassium vanadate thus generated was filtered and the filtrate was added to the above suspension with stirring. This stirring was continued to next 6 h while adjusting the pH of the reaction mixture slowly to ca. 6.5. The reddish-brown resin beads were filtered off, washed with water followed by ethanol and dried in air oven at ca. 100 °C where reddish-brown beads slowly changed to green due to reduction of dioxovanadium(V) complex to oxovanadium(IV). Obs. for PS-[VO(saldien)]: C, 63.46%; H, 6.16%; N, 5.66%; V, 4.2%.

2.3.3. PS-[Cu(saldien)] (2)

Polymer-anchored ligand PS-H$_2$saldien (3.5 g, 4.93 mmol equiv. of nitrogen) was allowed to swell in 20 ml of DMF for 2 h. A DMF solution (50 ml) of cupric acetate monohydrate (2.6 g, 13 mmol) was added to the above suspension and the reaction was heated at ca 80 °C in an oil bath with continuous stirring for 8 h. After cooling to room temperature, the reaction mixture was filtered off, washed with hot DMF followed by hot ethanol and dried in air oven at 120 °C. Obs. for [PS-Cu(saldien)]: C, 65.11%; H, 6.33%; N, 5.73%; Cu, 6.43%.

2.3.4. [VO(saldien)] (3)

Salicylaldehyde (2.44 g, 20 mmol) and diethylenetriamine (1.03 g, 10 mmol) were dissolved in 40 ml of dichloromethane and stirred at ambient temperature for 1 h. After addition of anhydrous Na$_2$SO$_4$ (1.0 g) to the above solution, it was further stirred for next 2 h and filtered. To the filtrate [VO(acac)$_2$] (2.65 g, 10 mmol) was added in one portion and the reaction mixture was stirred for 4 h The separated green solid was filtered off, washed with diethyl ether and dried in vacuum desiccator. Yield 60%. Obs.: C, 57.2%; H, 4.98%; N, 11.03%. Calcd. for C$_{18}$H$_{19}$N$_3$O$_3$V: C, 57.61%; H, 4.83%; N, 11.20%.

2.3.5. [Cu(saldien)] (4)

Ligand H$_2$saldien was prepared in situ in dichloromethane as stated above and to this was added CuCl$_2$·2H$_2$O (1.70 g, 10 mmol) dissolved in 20 ml of dichloromethane. After stirring the reaction mixture at room temperature for 4 h, the volume of the solvent was reduced to ca. 20 ml where a green solid slowly precipitated out within 4 h. This was filtered off, washed with diethyl ether and dried in vacuum desiccator. Yield 45%. Obs.: C, 58.02%; H, 4.61%; N, 11.11%. Calcd. for C$_{18}$H$_{19}$N$_3$O$_2$Cu: C, 58.13%; H, 4.88%; N, 11.30%.

2.4. Catalytic activity

2.4.1. Oxidation of phenol

In a typical reaction, phenol (1.88 g, 20 mmol) was dissolved in 10 ml of water in 50 ml of double necked round bottom flask and to this 30% H$_2$O$_2$ (2.28 g, 20 mmol) and PS-[VO(saldien)] or PS-[Cu(saldien)] (30 mg) were added. The reaction was carried out at 70 °C and the progress of the reaction was monitored by withdrawing small aliquots of the reaction mixture periodically and analyzing quantitatively by Thermoelectron gas-chromatograph having HP-1 capillary column (30 m × 0.25 mm × 0.25 μm) and FID detector. Standard solution of phenol, catechol and *p*-benzoquinone were used externally for calibration.

2.4.2. Oxidation of hydroquinone

Oxidation of HQ was carried out in a 50 ml of flask by charging hydroquinone (0.55 g, 5 mmol), 30% H$_2$O$_2$ (1.14 g, 10 mmol), PS-[VO(saldien)] or PS-[Cu(saldien)] (30 mg) in 10 ml of acetate buffer as the reaction medium. The reaction was carried out at room temperature and progress was monitored through UV–vis spectrophotometer. The percent conversion of

hydroquinone to *p*-benzoquinone was calculated through calibration plot method.

3. Result and discussion

3.1. Synthesis and characterisation of catalysts

Ligand, H$_2$saldien obtained by the condensation of salicylaldhyde and diethyleletriamine reacts with chloromethylated polystyrene (18.9% Cl, 5.35 mmol Cl/g resin) crosslinked with 5% divinylbenzene in DMF in the presence of triethylamine and ethylacetate to give polystyrene supported ligand, PS-H$_2$saldien. In the process of anchoring, the NH group of H$_2$saldien reacts with –CH$_2$Cl as shown in Scheme 2. Previously we have reported anchoring of 2-(α-hydroxy)methylbenzimidazole (Hhmbmz) and 2-(α-hydroxyethyl)benzimidazole(Hhebmz) to chloromethylated polystyrene through NH group of the benzimidazole moiety [34]. At least 80 °C was required temperature for effective anchoring. Miller and Sherrington have used refluxing toluene for anchoring of organic ligand through NH group to the chloromethylated polystyrene [35]. Joseph and Halligudi have anchored [VO(saldien)] on to fuctionalized SBA-15 through NH of the imine group [31]. The remaining chlorine content of 1.43 mmol/g resin in the anchored ligand suggests roughly 70% conversion with respect to the available chloromethyl group.

The reaction of potassium vanadate, generated in situ by dissolving V$_2$O$_5$ in an aqueous solution of KOH, with the anchored ligand, PS-H$_2$saldien and adjusting pH of the reaction mixture to ca. 6.5 results in the formation of unstable polymer-anchored dioxovanadium(V) species that converts slowly to oxovanadium(IV) complex PS-[VO(saldien)] (1) during drying process. Slow transformation of oxovanadium(V) complex of *N*-(2-phosphonomethyl)iminodiacetic acid (H$_4$pida) to stable oxovanadium(IV) complex, Na$_4$[{VO(pida)}$_2$] has earlier been noted in solution where NaVO$_3$, an oxovanadium(V) starting material, was used [36]. The polymer anchored complex, PS-[Cu(saldien)] (2) was synthesised by reacting anchored ligand with cupric acetate in DMF. The whole synthetic procedures are presented in Scheme 3. In complexes 1 and 2, the ligand:metal stoichiometry ratio was found to be 1.63:1 and 1.25:1, respectively, that clearly shows the metal% conversion of 61% and 71.63%, respectively. The relevant analytical data of ligand and complexes are presented in Table 1. Thermogravimetric analyses of both the complexes in oxygen atmosphere show that they are thermally stable up to 200 °C and there after slowly decompose exothermally in multiple steps. Quantitative measurement of weight loss at various steps was not possible due to their overlapping nature.
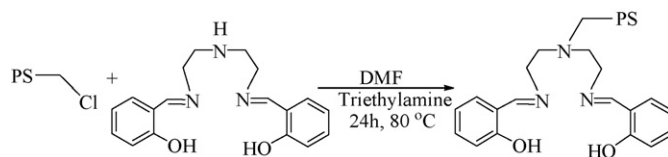
Scheme 2. Reaction scheme for the synthesis of PS-H$_2$saldien; PS represents the backbone of the chloromethylated polystyrene.
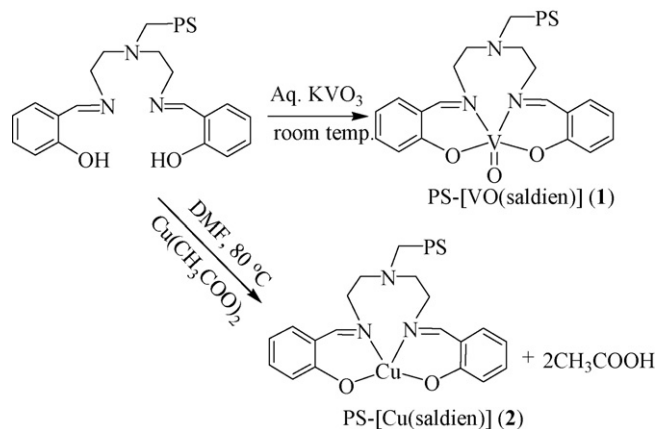
Scheme 3. Reaction scheme for the preparation of PS-[VO(saldien)] and PS-[Cu(saldien)] and their proposed structure.

3.1.1. Spectral studies

The chloromethylated polystyrene shows strong peaks at 1264 and 673 cm^{-1} [37] in the IR spectrum and absence of these peaks in PS-H$_2$saldien suggests the covalent bonding of chloromethylated polystyrene with H$_2$saldien (cf. Scheme 2). This is further supported by the absence of ν(NH) band appearing at 3060 cm^{-1} in H$_2$saldien. The presence of multiple bands of medium intensity covering the 2800–2900 cm^{-1} regions suggests the existence of –CH$_2$ group. A broad band in the 2550–2700 cm^{-1} regions in H$_2$saldien is assigned due to intramolecular hydrogen bonding between phenolic–OH and the nitrogen of azomethine/secondary amine. Absence of this band in polymer-anchored complexes suggests the breaking of hydrogen bonding followed by coordination of phenolic oxygen after proton replacement. This is further supported by the absence of ν(OH) band in ca. 3500 cm^{-1} region. A band corresponding to ν(C=N) at 1630 cm^{-1} in PS-H$_2$saldien shifts to lower wave number thereby indicating the coordination of azomethine nitrogen to the metal ions. The appearance of 2–4 bands in the low frequency region (400–500 cm^{-1}) also suggests the coordination of nitrogen and oxygen to the metal ion. Neat complexes [VO(saldien)] and [Cu(saldien)] exhibit very similar spectral bands. The non-involvement of nitrogen of the NH group in coordination is indicated by the presence of ν(NH) at 3230 cm^{-1} in [VO(saldien)] and at 3140 cm^{-1} in [Cu(saldien)]. The existence of free NH group in [Zn(saldien)] has been established on the basis of ^{1}H NMR study [30]. In addition, PS-[VO(saldien)] and [VO(saldien)] exhibit a medium intensity band at 930 and 927 cm^{-1} due to ν(V=O) and this indicates the presence of vanadium at the centre.
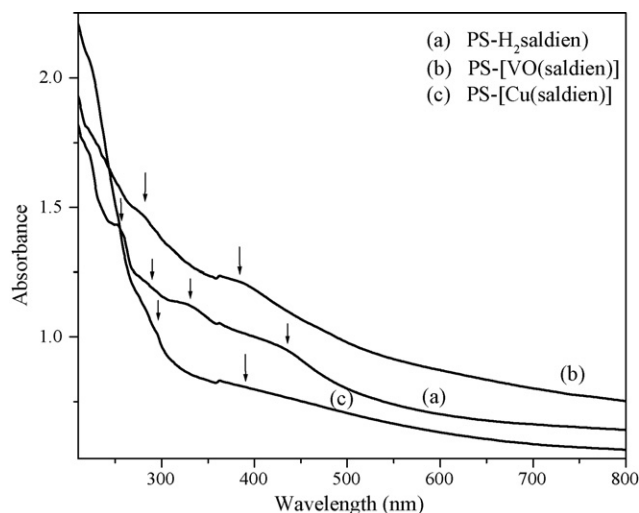

Fig. 1. Electronic spectra of PS-H$_2$saldien (a), PS-[VO(saldien)] (b) and PS-[Cu(saldien)] (c) recorded in Nujol.

Fig. 1 presents electronic spectra of polymer-anchored ligand and complexes, spectral data in Table 2. The spectrum of H$_2$saldien exhibits four bands at 402, 316, 255 and 220 nm. The polymer-supported ligand, PS-H$_2$saldien also exhibit the same number of bands with slightly shift in their position as compared to H$_2$saldien. The bands at 255 and 220 nm are assignable to π–π^* and ϕ–ϕ^* transitions, respectively, while the first two bands seem split band of n–π^* transition. A weak shoulder band also appears at ca. 280 nm, which is assigned as intra molecular hydrogen bonding. Absence of shoulder band in the spectra of all complexes suggests the destruction of hydrogen bonding and coordination of phenolic hydrogen to metal centre. Other bands are also observed in neat as well as supported complexes. The band at ca. 360 nm (in copper complexes) and 388 nm (in vanadium complexes) has been assigned due to ligand to metal charge transfer (lmct) band. While no other bands could be located in polymer-anchored complexes due to the poor loading of metal complexes, a new band at 625 nm (in neat [Cu(saldien)]) and 660 nm (in neat [VO(saldien)]) is assigned due to d–d transition. The spectral patterns of neat as well as anchored copper(II) complexes compare well with the zeolite-encapsulated [Cu(saldien]-Y and [Cu(salpn)]-Y, where square planar structure have been suggested. A square pyramidal structure has been suggested for [VO(saldien)] supported on SBA-15 on the basis of spectral studies [31]. We expect similar structure for anchored complex, PS-[(VO(saldien)] as similar spectral patterns were also observed for this.

Table 1
Physical data of ligands and complexes

Compound	Ligand loading	Metal ion loading	Ligand: metal ratio	Metal conversion (%)
PS-saldien	1.41	–	–	–
PS-[Cu(saldien)]	1.27	1.01	1.25:1	71.63
PS-[VO (saldien)]	1.35	0.82	1.63:1	61.0

Table 2
Electronic spectral data

Compounds	Solvent	λ_{max} (nm)
H$_2$saldien	MeOH	402, 316, 280, 255, 220
PS-H$_2$saldien	Nujol	407, 330, 284, 258, 222
PS-[Cu(saldien)]	Nujol	360, 278, 223, 205
[Cu(saldien)]	MeOH	625, 362, 267, 240, 223
PS-[VO(saldien)]	Nujol	388, 287, 228, 219
[VO(saldien)]	MeOH	660, 388, 314, 254, 206

Scheme 4. Oxidation products of phenol.
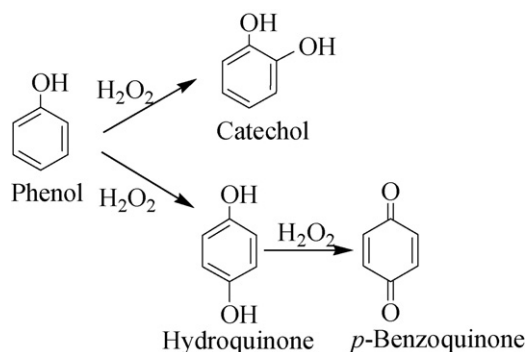
3.1.2. Scanning electron micrographs studies

Scanning electron micrographs (SEM) of pure chloromethylated polystyrene, anchored ligand PS-H$_2$saldien and polymer-anchored complexes were recorded taking single bead of each to understand the morphological changes occurring at various levels of syntheses. A light roughening of the top layer of bead having polymer-anchored ligand as compared to relatively smooth and flat surface of neat polystyrene bead suggests the change of nature of bead on covalent bonding. Images of metal complex beads show further roughening of the top layer which is possibly due to interaction of metal ions with ligand to arrange in the fixed geometry of the complex. Accurate information on the morphological changes in terms of exact orientation of ligand coordinated to the metal ion has not been possible due to poor loading of the metal complex.

3.2. Catalytic activity

3.2.1. Oxidation of phenol

Oxidation of phenol, generally, gives catechol and hydroquinone as major products. These are the expected products according to the directing effect of the phenolic OH group. However, subsequent oxidation of hydroquinone may provide benzoquinone; Scheme 4. In the present investigation, we have studied the oxidation of phenol catalysed by polymer-anchored complexes using H$_2$O$_2$ as oxidant in aqueous medium and only two products namely catechol and *p*-benzoquinone were identified. This reflects the fact that hydroquinone formed in the beginning is further oxidized to benzoquinone.

We have optimised the reaction conditions to achieve better selectivity for the formation of *p*-benzoquinone along with the maximum oxidation of phenol. Thus, catalysts PS-[Cu(saldien)] was taken as a representative and the effect of amount of catalyst, effect of H$_2$O$_2$ concentration (moles of H$_2$O$_2$ per mole of phenol), effect of temperature and volume of solvent have been studied.

3.2.1.1. Effect of H$_2$O$_2$ concentration.
The oxidation of phenol is dependent of the amount of oxidant H$_2$O$_2$ used during reaction. As shown in Fig. 2, at a H$_2$O$_2$ to phenol molar ratio of 1:1 for the fixed amount of phenol (1.88 g, 20 mmol), PS-[Cu(saldien)] (30 mg) and temperature (70 °C) in 10 ml of water, only 9.4% conversion was achieved in ca. 4 h of contact time. Increasing
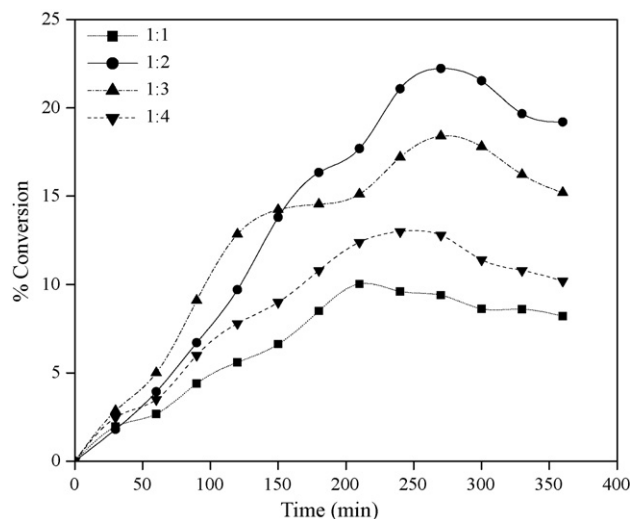

Fig. 2. Effect of H$_2$O$_2$ concentration on phenol oxidation, reaction conditions: phenol (1.88 g, 20 mmol), PS-[Cu(saldien)] (30 mg), temperature 70 °C and water (10 ml).

the ratio to 1:2 increases the conversion to 22.2%. This conversion goes down to ca. 18% on further increasing the ratio. Table 3 analyses the percent conversion of phenol and selectivity of products formation after 4 h of reaction time. At lowest concentration (1:1) of oxidant the selectivity for the *p*-benzoquinone was highest (82%) and started to take a decreasing trend (64.5% (at 1:2) <59.2% (at 1:3) <54.0% (1:4) with the increase of oxidant concentration. At the same time the selectivity of catechol formation went up from 17.0% to 44.0% on increment of H$_2$O$_2$ concentration. At highest conversion of phenol i.e. at 1:2 (phenol:H$_2$O$_2$) ratio the turn over rates per hour (TOFh^{-1}) was calculated to be 36.6 and goes down while increasing or decreasing this ratio. The trends of plots presented in Fig. 2 also give some useful information. For example, after ca. 4 h of contact time, all plots show decreasing trend of phenol conversion. In fact, the *p*-benzoquinone formed is slowly converted into GC silent polymeric material with time which affects on the net ratio of phenol and oxidation products at particular time. Evidences for the polymerization of *p*-benzoquinone at higher temperature and decreasing trend of phenol conversion in water have also been reported in the literature [38].

3.2.1.2. Effect of catalyst concentration.
For the fixed operating conditions of phenol (1.88 g, 20 mmol) and 30% H$_2$O$_2$ (4.56 g,

Table 3
Effect of H$_2$O$_2$ concentration on the conversion of phenol and selectivity of products[a]

Phenol: H$_2$O$_2$ ratio	Conversion (%)	TOF (h^{-1})[b]	Product selectivity (mol%)	
			p-Benzoquinone	Catechol
1:1	9.4	15.5	82	17.0
1:2	22.2	36.6	64.5	34.6
1:3	18.4	30.2	59.2	40.0
1:4	18.0	29.5	54.0	44.0

[a] For reaction conditions see Fig. 2.
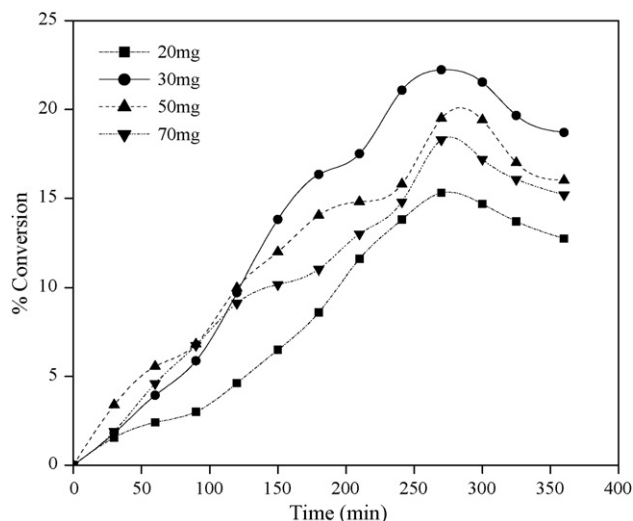[b] TOF (h^{-1}) = no. of moles of substrate converted per mole of catalyst in 1 h.

Fig. 3. Effect of amount of catalyst on the phenol oxidation, reaction conditions: phenol (1.88 g, 20 mmol), H_2O_2 (4.56 g, 40 mmol), temperature 70 °C and water (10 ml).
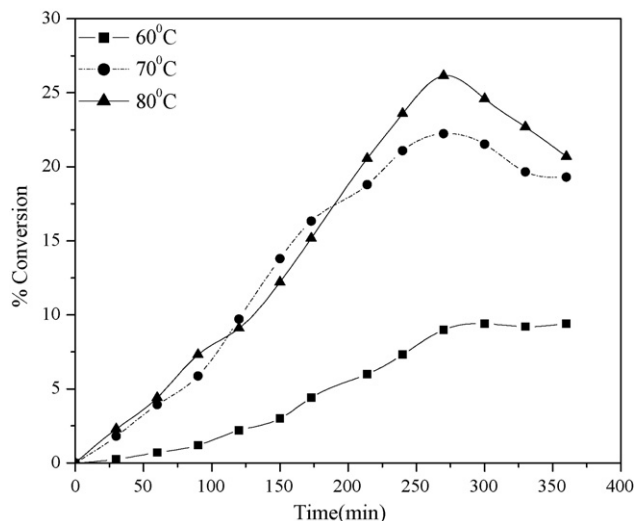

Fig. 4. Effect of temperature on the oxidation of phenol, reaction conditions: phenol (1.88 g, 20 mmol), H_2O_2 (4.56 g, 40 mmol), PS-[Cu(saldien)] (30 mg) and water (10 ml).

40 mmol), four different amounts of catalyst viz. 20, 30, 50 and 70 mg were used in 10 ml of water and reaction was carried out at 70 °C. As shown in Fig. 3, maximum conversion of 22.2% was obtained with 30 mg of catalyst. Decreasing or increasing the amount of catalyst did not improve the conversion; Table 4 lists details of conversion and products distribution. While decrease in conversion at lower concentration of catalyst may be attributed due to the presence of fewer catalytic centres, the rapid decomposition of H_2O_2 at higher concentration of catalysts may be responsible for the poor conversion of phenol. A lower trend of all plots again in Fig. 3 after ca. 4 h of reaction time is due to polymerization of part of the *p*-benzoquinone formed during reaction.

3.2.1.3. Effect of temperature. As shown in Fig. 4, temperature has great influence on the performance of the catalyst for phenol conversion as well as selectivity of the products. For example, running the reaction at 60 °C for the fixed amount of phenol (1.88 g, 20 mmol) and 30% H_2O_2 (4.56 g, 40 mmol) in 10 ml of water gave only about 10% conversion. This conversion was increased to 22.2% when reaction was carried out at 70 °C and to 26.4% at 80 °C. However, in terms of the selectivity of different products, selectivity of the formation of *p*-benzoquinone is much higher at 70 °C (ca. 65%) and goes down to 36.86 at 80 °C; Table 5 provides details of conversion and products selectivity

at different temperature. A steep fall in net conversion was also noted at 80 °C after 4 h of reaction time and this suggests the faster conversion of *p*-benzoquinone to polymeric material at this temperature.

3.2.1.4. Effect of volume of solvent. Among several solvents such as water, acetonitrile, methanol and dichloromethane, water was found to be the most suitable reaction medium in terms of the *p*-benzoquinone selectivity. However, its volume has considerable influence on the conversion of phenol. As shown in Fig. 5, the conversion of phenol improves from 4.2% to 33.1% in 4 h of contact time on decreasing the amount of water from 20 to 2.5 ml under the reaction conditions fixed as above. However, the selectivity for *p*-benzoquinone decreases considerably from 73% to 10% and that of catechol increases from 27% to 90%. On balance, 10 ml of water was considered to be the sufficient enough to obtain the good selectivity of *p*-benzoquinone while maintaining the good conversion of phenol as well.

Thus, under the optimised conditions i.e. phenol (1.88 g, 20 mmol), H_2O_2 (4.56 g, 40 mmol), PS-[Cu(saldien)] (30 mg), temperature (70 °C) and water (10 ml), the reaction acquired steady state within ca. 4 h of reaction time with 22.2% conversion. Within the conversion, the yield of catechole was 14.4% and that of *p*-benzoquinone was 7.8%. The percent formation of *p*-bezoquinone and catechol under optimised conditions with

Table 4
Effect of catalyst amount on phenol oxidation after 4 h of reaction time[a]

Catalysts amount (mg)	Conversion (%)	TOF (h^{-1})	Product selectivity (mol%)	
			Benzoquinone	Catechol
20	15.3	37.8	68	30.7
30	22.2	36.6	64.5	34.6
50	19.5	19.3	67.7	32.3
70	18.3	12.9	60.0	39.5

[a] For reaction conditions see Fig. 3.

Table 5
Effect of temperature on phenol conversion[a]

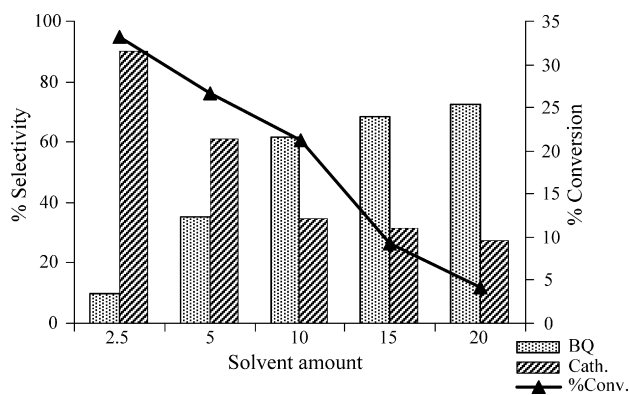| Temperature (C)	Conversion (%)	TOF (h^{-1})	Product selectivity (mol%)	
			p-Benzoquinone	Catechol
60	10.0	20.2	68.46	31.54
70	22.2	36.6	64.50	34.6
80	26.4	43.5	36.86	63.13
Room temperature	No reaction			

[a] For reaction conditions see Fig. 4.

Fig. 5. Effect of volume of water on the rate of the oxidation of phenol, reaction conditions: phenol (1.88 g, 20 mmol), H$_2$O$_2$ (4.56 g, 40 mmol), PS-[Cu(saldien)] (30 mg), temperature (70 °C).

respect to time is presented in Fig. 6. Yields of *p*-benzoquinone as well as catechol increases and then takes decreasing trend after ca. 4 h of reaction time. We have also analysed the percentage conversion of phenol and changes in the selectivity of products with time and the relevant profiles are presented in Fig. 7. It is clear from the profiles that the benzoquinone to catechol ratio is much high in the beginning. However, this ratio decreases with time and after ca. 4 h of reaction time it is ca. 2:1. After 4 h where conversion follows the decreasing trend, this ratio further goes down and finally takes opposite trend and percent selectivity of catechol dominates.

Catalyst PS-[VO(saldien)] under the above reaction conditions, has shown only 3% conversion of phenol, similar observations were also noted with neat [VO(saldien)]. This observation suggests that [VO(saldien)] is not able to react effectively with H$_2$O$_2$ in water to form intermediate peroxo species that can transfer oxygen to substrate for oxidation. On the other hand neat catalyst [Cu(saldien)] has performed better than its polymeric supported analogue and recorded 46.2% conversion. However,
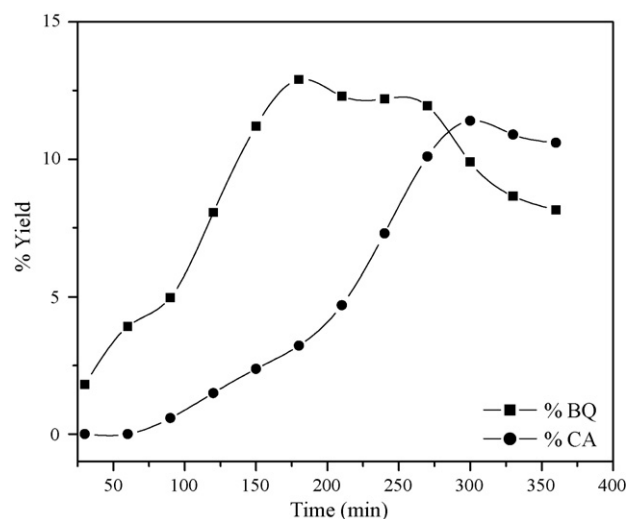

Fig. 6. Plots showing variation in the percentage yield of benzoquinone and catechol formation at 70 °C as a function of time. Other reaction conditions: phenol (1.88 g, 20 mmol), H$_2$O$_2$ (4.56 g, 40 mmol), PS-[Cu(saldien)] (30 mg) and water (10 ml).
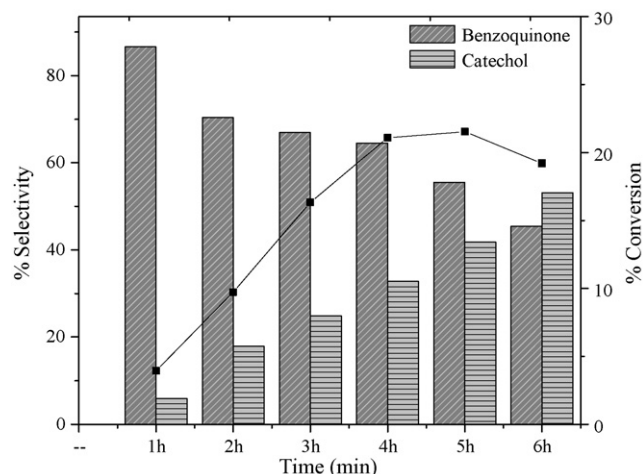

Fig. 7. Bar diagram showing percentage selectivity of benzoquinone and catechol formation and plot showing percentage conversion of phenol as a function of time. Reaction conditions: phenol (1.88 g, 20 mmol), H$_2$O$_2$ (4.56 g, 40 mmol), PS-[Cu(saldien)] (30 mg), temperature 70 °C and water (10 ml).

the obtained products were only catechol and hydroquinone with 29.8% and 16.4% yield, respectively. The catalytic performances of all catalysts, the yield of products and their selectivity are summarised in Table 6.

Effects of other solvents have also been tested and results are summarized in Table 7. Acetonitrile, as shown in Table 7, also favours fairly good conversion of phenol but catalysts generally give catechol and hydroquinone with highest selectivity towards catechol and lowest to *p*-benzoquinone. But, methanol has not been found to be a good solvent as percentage conversion of phenol is very poor in it.

The catalytic performance of the polymer-anchored vanadium complex reported here compares well with the data reported in the literature. For example, polymer-anchored complexes, PS-[VO(sal-ohyba).DMF (33.8%) (H$_2$sal-ohyba = Schiff base derived from salicylaldehyde and *o*-hydroxybenzyl amine) [39], PS-K[VO(O$_2$)$_2$(2-pybzm)] (2-pybzm = 2-(2-pyridylbemzimidazole))(33.5%) [34], zeolite-encapsulated [VO(salen)] (H$_2$salen = *N*,*N*′-bis(salicylidene)ethane-1,2-diamine) (32.6%) [29] and NH$_4$[VO$_2$(sal-inh)] (H$_2$sal-inh = Schiff base derived from salicylaldehyde and isonicotinic acid hydrazide) (26.5%) [40], and polymeric [–CH$_2${VO(salen)}–]$_n$ (38.6%) [41] are close to that reported for PS-[VO(saldien)] in acetonitrile, though, they differ in their selectivity towards the formation of catechol and hydroquinone. The performance of PS-[VO(saldien)] is poor in water but the product is benzoquinone selectively.

Polymer-anchored copper complex has also shown relatively less conversion (34.2%) than zeolite-encapsulated [Cu(saldien)]-Y (46.0%) but better than [Cu(salpn)]-Y (31.0%) in acetonitrile, the obtained selectivity for catechol and hydroquinone is, however, comparable. The selectivity as well as conversion both differs in water. With only 22.2% conversion in water, it is more selective towards the formation of benzoquinone (64.5%) and less towards catechol (34.6%), and no formation of hydroquinone was observed.

Table 6
Percentage conversion of phenol catalysed by various catalysts and selectivity of the reaction products

Catalysts/amount	Conversion (%)	TOF (h^{-1})	Selectivity (yield) of products (%)[a]		
			BQ	CA	HQ
PS-[Cu(saldien)], 30 mg	22.2	36.6	64.9 (14.4)	35.1 (7.8)	–
[Cu(saldien)], 11.28 mg	46.2	76.2	–	64.6 (29.8)	35.4 (16.4)
Ps-[VO(saldien), 37 mg	3.1	5.1	100 (3.1)	–	–
[VO(saldien)], 11.5 mg	1.0	–	100 (1)	–	–

[a] BQ: *p*-benzoquinone; CA: catechol; HQ: hydroquinone. Reaction conditions: phenol (1.88 g, 20 mmol), 30% H_2O_2 (4.56 g, 40 mmol), water (10 ml), temperature 70 °C.

Table 7
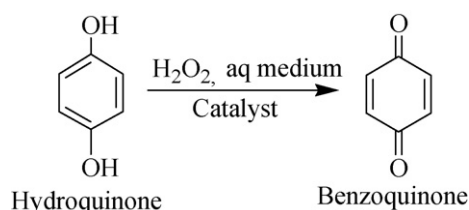Effect of different solvents on the oxidation of phenol

Catalysts	Solvent	Conversion (%)	Product selectivity (mol%)		
			CA	HQ	BQ
PS-[Cu(saldien)], 30 mg	CH_3CN	34.2	66.0	21.8	12.2
	CH_3OH	5.2	–	–	100
PS-[VO(saldien)], 37 mg	CH_3CN	36.8	58.1	40.0	1.9
	CH_3OH	2.7	–	–	100

Reaction conditions are same as in Table 6.

3.2.2. Oxidation of hydroquinone

Oxidation of hydroquinone to benzoquinone is a well known reaction occurring in nature, Scheme 5. In aqueous medium the rate of auto oxidation of hydroquinone is pH dependent, occurring comfortably in slightly alkaline solution (pH 7.3–7.0) to give dark brown solution. Slow oxidation of hydroquinone has also been noted in neutral solution. Kinetics of hydroquinone oxidation has been reported in acetate and phosphate saline buffer [28]. We have studied the oxidation of hydroquinone catalysed by polymer-anchored catalysts PS-[Cu(saldien)] and PS-[VO(saldien)] at different pHs using H_2O_2 as an oxidant and the formation of benzoquinone was monitored by electronic absorption spectrophotometer as a function of time. As hydroquinone absorbs at $\lambda_{max} = 289$ nm while *p*-benzoquinone does not show any peak in this region, the decrease in absorption maximum due to the formation of *p*-benzoquinone was recorded after withdrawing small aliquot from the reaction mixture at different time intervals. Fig. 8 shows successive decrease in absorption maximum as a function of time as a result of the oxidation of hydroquinone for one of the catalytic runs.

Three different buffer solutions (10 ml) namely, acetate, phosphate and carbonate buffers having pH 4.64, 6.85 and 10, respectively, were considered while fixing the amount of hydroquinone (0.55 g, 5 mmol), 30% H_2O_2 (1.14 g, 10 mmol) and PS-[Cu(saldien)] (30 mg). The reaction was monitored by

UV–vis spectrophotometer at room temperature while recording the decrease in the absorption maximum as mentioned above and % conversion was calculated through calibration plot.

Data presented in Table 8 for the reaction carried out at different pHs shows that conversion increases on increasing the pH of the reaction medium. In case of acetate buffer (pH 4.64), the maximum conversion was 61.3% in 3 h of contact time while phosphate buffer (pH 6.85) improved this conversion from 63.1% to 93.0% in 3 h. The carbonate buffer (pH 10) has shown remarkable result. Here, reaction reaches to the equilibrium within 1 h of the reaction time with 90.2% conversion. Thus, the pH 10 seems to be the best suited one to obtained maximum oxidation followed by pH 6.85 while pH 4.64 has shown the poorest result.
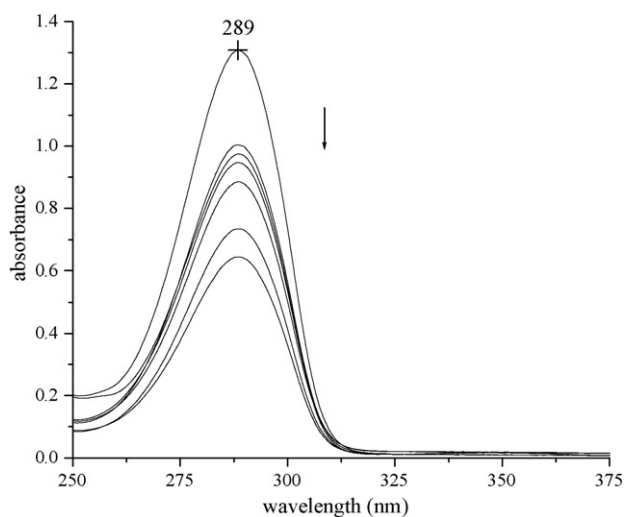

Fig. 8. Decrease in the absorption maximum for PS-[Cu(saldien)] catalysed oxidation of hydroquinone in phosphate buffer. Spectra were recorded during 3 h of reaction time.

Scheme 5. Oxidation product of hydroquinone.

Table 8
Effect of pH on hydroquinone oxidation

Time (h)	Conversion (%)		
	Acetate buffer (pH 4.64)	Phosphate buffer (pH 6.85)	Carbonate buffer (pH 10)
0.5	51	63.1	64.7
1.0	54.4	72.1	90.2
1.5	56.4	85.6	90.2
2.0	58.3	86.9	90.2
2.5	60.3	92.7	90.0
3.0	61.3	93.0	90.0

Reaction conditions: hydroquinone (0.55 g, 5 mmol), 30% H_2O_2 (1.14 g, 10 mmol), PS-[Cu(saldien)] (30 mg), buffer solution (10 ml).

We have also tested the effect of H_2O_2 concentration on the rate of oxidation of hydroquinone in carbonate buffer. Results show that increasing the amount of hydroquinone to H_2O_2 molar ratio to 1:3 improved the oxidation of hydroquinone to 98.1% in 30 min. A total of 100% conversion could only be achieved with 1:6 (hydroquinone:H_2O_2) molar ratio in 30 min of reaction time. Thus, the suitable reaction conditions at room temperature for the maximum oxidation of hydroquinone in carbonate buffer may be given as: hydroquinone (0.55 g, 5 mmol), 30% H_2O_2 (1.71 g, 15 mmol), PS-[Cu(saldien)] (30 mg) and carbonate buffer solution (10 ml). It is important to note that kinetics of the oxidation of hydroquinone has been reported in the literature considering hydroquinone to oxidant ratio of 1:10 [28].

Under the above conditions catalyst PS-[VO(saldien)] has shown only 16.6% conversion. Neat complexes i.e. [Cu(saldien)] and [VO(saldien)] have also shown very poor result (Table 9). However, in all cases only benzoquinone formation was noted. Amongst all catalysts, the turn over rates of 321.6 is comparatively also high for catalyst PS-[Cu(saldien)].

3.2.3. Possible reaction pathway of the catalysts, their heterogeneity and recyclability

In order to establish possible reaction pathway, the methanolic solutions of the neat complexes [Cu(saldien)] and [VO(saldien)] were treated with H_2O_2 dissolved in methanol and the progress of the reaction was followed by electronic absorption spectroscopy. Thus, the addition of one-drop portions of 30% H_2O_2 dissolved in methanol to 10 ml of ca. 10^{-4} M solution of [Cu(saldien)] causes a gradual shift of 361–370 nm along with decrease in band maximum while 270 nm band shows only sharp decrease in band maximum, Fig. 9. The band

Table 9
Percentage conversion of hydroquinone and selectivity of *p*-benzoquinone

Compound	Catalyst weight (mg)	Conversion (%)	TOF (h^{-1})	*p*-Benzoquinone (mol%)
PS-[Cu(saldien)]	30.0	98.1	321.6	100
[Cu(saldien)]	11.3	19.6	64.2	100
Ps-[VO(saldien)]	37.0	16.6	54.4	100
[VO(saldien)]	11.5	17.4	57.0	100

Reaction conditions: hydroquinone (0.55 g, 5 mmol), carbonate buffer (10 ml), 30% H_2O_2 (1.7 g, 15 mmol).
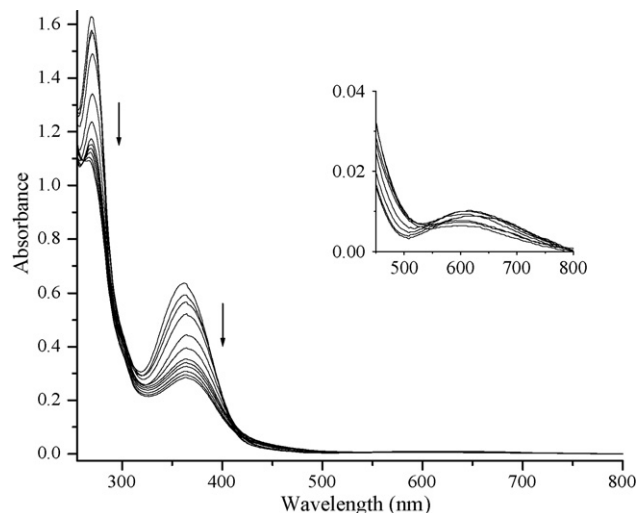

Fig. 9. Titration of [Cu(saldien)] with H_2O_2. Spectra were recorded after the successive addition of one drop portions of H_2O_2 dissolved in methanol to 10 ml of ca. 10^{-4} M solution of [Cu(saldien)].

appearing due to d–d transition at 625 nm also records only slight decrease in intensity. All these suggests the interaction of peroxo group with Cu(II) centre. At least three types of intermediates having copper–oxygen interaction viz. side-on Cu^{III}-(μ-η^2-peroxo)-Cu^{III}, bis(μ-oxo-Cu^{III}) and Cu^{III}–O–O–H (copper-hydroperoxide) have been reported in the literature during catalytic action [42]. The facile formation, due to vacant site, of [(HOO)–Cu(saldien)] intermediate is expected in PS-[Cu(saldien)] as metal centers in the polymer-supported complexes are well separated. This intermediate transfers the coordinated oxygen atoms to the substrates to obtain the products. Thus, the catalytic performance of supported catalyst could be attributed to the formation of facile and reversible intermediate species. A shift of d–d transition from 625 nm towards lower wave number without isosbestic point in neat complex hints the merging of the d–d band with additional charge transfer band due to Cu-hydroperoxide complex formation; a characteristic charge transfer band due to Cu-hydroperoxide is known to appear around 600 nm [43]. Based on observed reaction products, however, the mode of action of Cu-hydroperoxide in the oxidation seems to be solvent dependent and also differs in neat and supported complexes.

Similarly titration of ca. 0.5×10^{-3} M methanolic solution of [VO(saldien)] with H_2O_2 dissolved in methanol causes increase in the intensity of 380 nm band. At the same time the UV band at 314 nm marginally shifts to 319 nm along with decrease in intensity, Fig. 10. The weak broad band appearing at 660 nm (not shown here) due to d–d transition slowly disappears. Such changes have been interpreted due to the generation of oxoperoxovanadium(V) species. Such oxoperoxovanadium(V) species for complexes [VO(sal-phen)] (H_2sal-phen = ligands derived from salicylaldehyde and *o*-phenylenediamine) [44] and [VO(sal-dach)] (H_2sal-dach = Schiff bases derived from salicylaldehyde and 1,2-diaminocyclohexane) [45] have been generated previously under similar condition. The peroxo complex, thus formed, transfers one of its oxygen to the substrate.
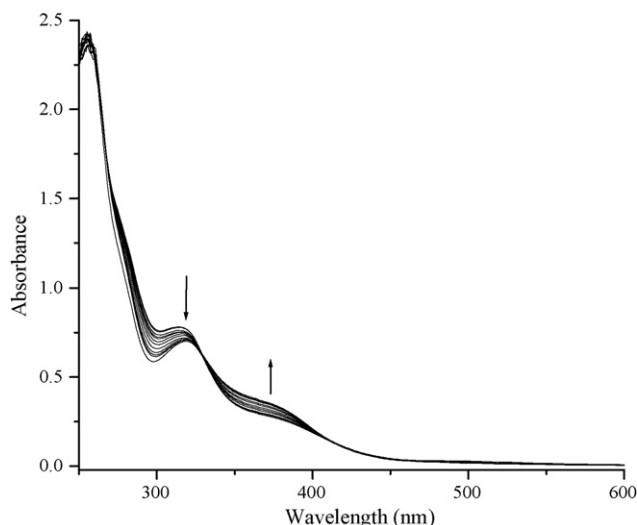
Fig. 10. Titration of [VO(saldien)] with H_2O_2. Spectra were recorded after the successive addition of one drop portions of H_2O_2 dissolved in methanol to 10 ml of ca. 0.5×10^{-3} M solution of [VO(saldien)].

Changing of bead's colour from green to red can also be visualized during catalytic reaction and this is possibly due to the formation of dioxovanadium(V) species via peroxo complex generation. But the recovered beads on drying slowly gain their original green colour i.e. stabilize only as oxovanadium(IV) species.

Recycle ability experiments were performed by separating the catalysts from the reaction mixture after 4 h of contact time. After washing with acetonitrile and drying at 100 °C, the catalysts were subjected to another cycle under similar optimised reactions. Nearly same percentage of phenol conversion as observed in the first cycle suggests that copper and vanadium centres are intact with the ligand and catalytic potentialities of the catalysts are maintained. A blank reaction was also carried out using catalyst PS-[Cu(saldien)] or PS-[VO(saldien)] (30 mg), 30% H_2O_2 (20 mmol), water (10 ml) at 70 °C for 3 h. The absence of copper or vanadium in the filtrate suggests no leaching during catalytic reaction.

4. Conclusion

Polymer-anchored complexes PS-[Cu(saldien)] and PS-[VO(saldien)] have been prepared and used for the catalytic oxidation of phenol and hydroquinone. Various reaction conditions have been optimised to obtain maximum reaction product(s). It has been demonstrated that solvent plays an important role in altering the selectivity of reaction products. In acetonitrile, these catalysts are more selective towards the catechol and hydroquinone formation upon the oxidation of phenol. However, in water, they become more selective towards catechol and p-benzoquinone with the high selectivity of the later one. The conversion of p-benzoquinone to polymeric materials has been noted with the elapse of time. At higher temperature (ca. 80 °C), this conversion speeds up while lower temperature (ca. 70 °C) is good to keep p-benzoquinone in solution for longer time. Amongst acetate, phosphate and carbonate buffer solutions car-

bonate buffer (pH 10) gives ca. 90% conversion of hydroquinone in 1 h while phosphate buffer (pH 6.85) takes 2.5 h to give such high conversion.

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