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Oxidation of Benzyl Alcohols by Polymer Supported V(IV) Complex Using O_2

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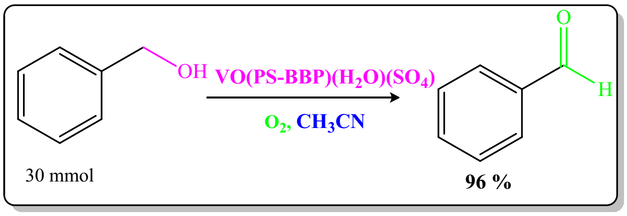
Abstract

Polymer supported and unsupported oxovanadium(IV) complexes with 2,6-bis(benzimidazolyl)pyridine were synthesized and characterized by elemental analyses, molar conductance, magnetic moment measurements, electronic, IR, ESR spectral studies, LC–MS and thermogravimetric analysis. Based on the results, an octahedral geometry was intended around V(IV) complexes. Polymer-anchored V(IV) complex catalyzed the oxidation of benzyl alcohols in acetonitrile with O_2 as an oxidant. Several parameters were differed to optimize the reaction conditions. Under the optimized reaction conditions, benzyl alcohol oxidation confirmed 96% conversion with 100% selectivity towards benzaldehyde. The developed catalyst revealed excellent benzyl alcohol oxidation at moderate temperature in presence of oxygen making the reaction simpler and environmentally benign. The polymer anchored V(IV) complex showed excellent recyclability as compared to its unsupported analogue.

Graphical Abstract



Keywords VO(BBP)(H_2O)(SO_4) · VO(PS–BBP)(H_2O)(SO_4) · Oxygen · Benzyl alcohol · Benzaldehyde

1 Introduction

Enormous potentiality of homogeneous transition metal complex catalysts in chemical transformations has increased attention in catalyst research, exploring numerous homogeneous complex-catalysts in oxidation reactions [1–3]. However, homogeneous catalysts suffer from several drawbacks related to the handling of sensitive metal–ligand complexes, deactivation during reaction and difficulty in recovery and reuse of expensive reagents, which hinders their practical applications in industrial processes. On the other hand, organic reactions using polymer-supported catalysts have received much attention because of easy workup and recyclability [4, 5].

Benzaldehyde is widely used in the pharmaceutical, dyeing, perfumery, and agrochemical industries [6]. Benzaldehyde is produced mainly via the routes of hydrolysis of benzyl chloride or oxidation of toluene [7, 8], however the former approach would face significant chlorine contamination while the latter would result in poor product selectivity with high temperature and pressure conditions. Therefore, liquid phase oxidation of benzyl alcohol (BzOH) to benzaldehyde is preferred and widely accepted [9, 10]. Several works have been carried out using homogeneous catalysts for BzOH oxidation [11–13], however heterogeneous catalysts are easily recovered and reused in BzOH oxidation, which is highly desirable in commercial application.

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Numerous supported metal catalyst systems involving Mn, Ru, Au and Pd have been used for the selective oxidation of BzOH [14–20] using oxidants such as TBHP, H_2O_2, O_2 [21–23] along with weak and strong bases [24, 25]. Conversely, these additives and conditions will affect purification and cause pollution [26, 27]. Thus, use of molecular oxygen as oxidant at lower temperatures has drawn much attention and widely accepted as a "greener" process for the production of benzaldehyde [28–30].

In the present work, we report the oxidation of BzOH using VO(PS–BBP)(H_2O)(SO_4) catalyst using cost effective and clean oxidant molecular oxygen at moderate temperature in acetonitrile. Operating parameters were varied; to understand catalyst behavior and improving its performance. The polymer supported vanadium complex showed better catalytic activity compared to its unsupported analogue towards oxidation of BzOH.

2 Experimental

2.1 Materials and Methods

All the chemicals used were of AR grade and purified by the standard methods [31]. The synthesized vanadium(IV) complexes were characterized by FT–IR, UV–Vis, ESR, LC–MS techniques, magnetic moment, and molar conductivity measurements, elemental and thermogravimetric analyses. The elemental analyses (carbon, hydrogen, oxygen and nitrogen) of the complexes VO(BBP)(H_2O)(SO_4) and VO(PS–BBP)(H_2O)(SO_4) was obtained from Elementar Vario Micro Cube CHNS analyzer. Diffuse reflectance spectra were recorded on $BaSO_4$ disks in Shimadzu UV–Vis–NIR model-3101P spectrophotometer. FT–IR spectra of solid compounds as KBr pellets were taken using Shimadzu 8400 s FT–IR spectrometer. Thermogravimetric analyses were carried out in TA instrument, SDT analyzer model Q600. Atomic absorption spectra (AAS) were recorded using Avanta Pm, GF 3000 instrument. LCMS measurements were recorded on LC–MSD-Trap-XCT-Plus. Magnetic moments of the complexes were measured by VSM model 7404. Molar conductivity measurement was carried out by using WTW conductivity meter. ESR measurements were carried out in solid state at room temperature in standard X band JES-FA200 spectrometer. Far IR spectrum was recorded on a Perkin-Elmer 1700-XFT instrument. SEM analysis is carried out using an ESEM Quanta 200, FEI.

2.2 Synthesis of VO(BBP)(H_2O)(SO_4) and VO(PS–BBP)(H_2O)(SO_4)

The polymer support used is chloromethylated polystyrene cross-linked with 6.5% divinylbenzene. The chloride content in the polymer support (PS) was found to be 9.6% by Volhard's method. 2,6-Bis(benzimidazolyl)pyridine (BBP) and functionalized polymer were synthesized as described earlier [32, 33]. Equimolar quantities (1 mmol) of 0.18 g $VOSO_4·XH_2O$ and 0.31 g BBP (1 mmol) were dissolved separately in ethanol (10 mL), mixed and refluxed on water bath for 4–6 h. After cooling to room temperature, a grey colored complex was formed and filtered, washed with ethanol, and finally dried over calcium chloride. Yield: 93%. The resulting unsupported vanadium complex VO(BBP)(H_2O)(SO_4) (Scheme 1a) is grey colored solid, air stable and insoluble in water and common organic solvents, but soluble in DMF and DMSO.

10 mL ethanol was added to 1 g of functionalized polymer (PS–BBP) at RT and kept for 1 h. To it, $VOSO_4·XH_2O$ (1 mmol; 0.17 g) in 10 mL of ethanol was added and stirred at reflux condition for 48 h. The resulting turkish blue colored polymer supported complex VO(PS–BBP)(H_2O)(SO_4) (1.5 g) (Scheme 1b) was filtered, Soxhlet extracted with ethanol and dried for 24 h at 100 °C.

2.3 Procedure for Benzyl Alcohol Oxidation

A typical VO(PS–BBP)(H_2O)(SO_4) catalyzed oxidation was performed. BzOH (30 mmol), VO(PS–BBP)(H_2O)(SO_4) (50 mg, 0.0995 mmol) and CH_3CN (5 mL) were placed in 100 mL three-neck round bottom flask fitted with a condenser, oxygen was bubbled through the reaction mixture at 60 °C for 4 h (Scheme 2). An aliquot of the reaction mixture was taken at various time intervals and analyzed by a Shimadzu GC-2010 gas chromatograph with flame ionization detector. The recovered VO(PS–BBP)(H_2O)(SO_4) was washed, dried in vacuo and reused.

3 Results and Discussion

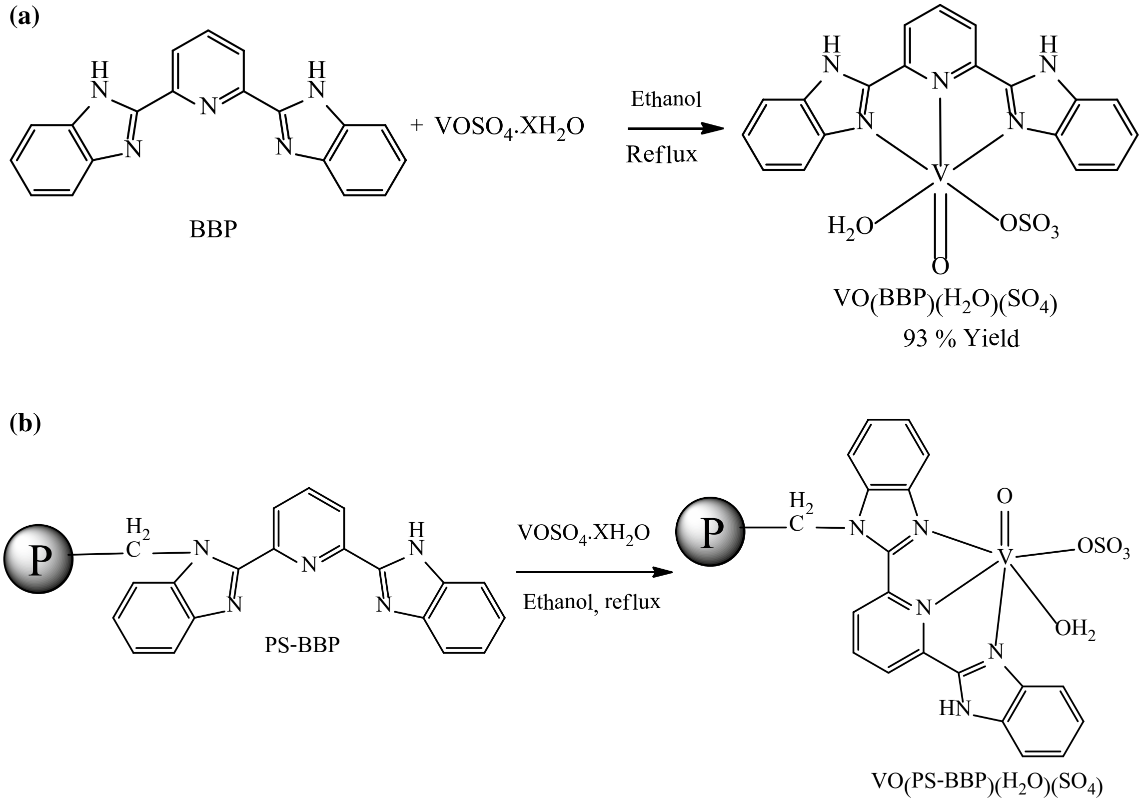
3.1 Catalyst Characterization

3.1.1 CHN Analyses

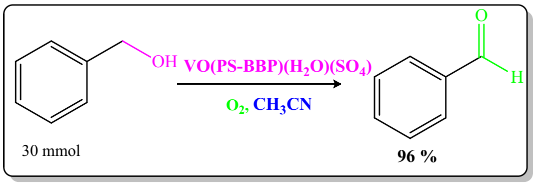
The CHN and vanadium content in the complexes are listed in Table 1, indicating 1:1 (metal:ligand) stoichiometry. The molar conductivity of VO(BBP)(H_2O)(SO_4) complex in DMF (~ 10^{-3} M) solution at room temperature was 19 S cm^2 mol^{-1}, signifying its non-electrolytic nature.

3.1.2 IR Spectral Studies

The IR spectrum of the chloromethylated polystyrene beads exhibited peaks at 1267 and 829 cm^{-1} due to ν(CH_2–Cl) and ν(C–Cl) respectively. On functionalization, ν(CH_2–Cl) and ν(C–Cl) decreased in intensity, in consistent with the



Scheme 1 **a** Synthesis of unsupported vanadium complex $VO(BBP)(H_2O)(SO_4)$. **b** Synthesis of polymer supported vanadium complex VO(PS–BBP)$(H_2O)(SO_4)$



Scheme 2 Oxidation of benzyl alcohol catalyzed by VO(PS–BBP)$(H_2O)(SO_4)$

bonding of BBP onto the polymer support. The free BBP exhibited a peak around 3190 cm^{-1} due to ν(N–H) and its intensity decreased and shifted to 2927 cm^{-1} in functionalized polymer indicating that one or two NH's groups of the benzimidazole moiety of the ligand may be deprotonated and bonded to polymer support (Fig. 1). The IR spectrum of $VO(BBP)(H_2O)(SO_4)$ is presented in Fig. 2. The complex revealed peaks at 3290, 3065 and 1319 cm^{-1} due to ν(O–H), ν(N–H) and ν(C–N) respectively. The ν(C=N) of BBP at 1615 cm^{-1} was shifted to lower energy by 10 cm^{-1} in the complex suggesting the coordination of tertiary nitrogens of BBP to VO^{2+} [33]. Peak at 970 cm^{-1} was due to the presence of ν(V=O). The peaks at 1462 and 1108 cm^{-1} were due to asymmetric and symmetric sulphate stretch of monodentately coordinated sulphate group in the complex [34].

Functionalized polymer PS–BBP exhibited peak due to ν(N–H) around 3190 cm^{-1} and the peak at 1623 cm^{-1} was assigned to ν(C=N) of benzimidazole/pyridine moieties in addition to polymer peaks [35]. The IR spectrum of VO(PS–BBP)$(H_2O)(SO_4)$ showed peaks due to ν(C=N)

Table 1 Analytical data and magnetic moments of supported and unsupported vanadium complexes

Compound	C %	H %	N %	V %	μ_{eff} (BM)
$VO(BBP)(H_2O)(SO_4)$	45.36 (46.35)	3.43 (3.07)	13.87 (14.22)	10.01 (10.35)	1.75
VO(PS–BBP)$(H_2O)(SO_4)$	76.30	8.72	5.09	5.6	1.73
Recycled VO(PS–BBP)$(H_2O)(SO_4)$	76.30	8.72	5.09	5.0	–

Calculated values are in parentheses

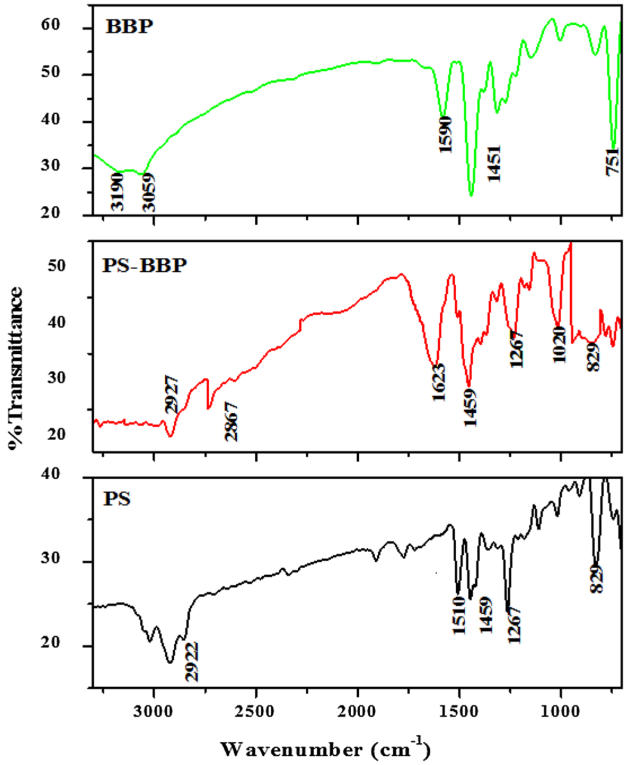


Fig. 1 FT–IR spectra of PS, BBP and PS–BBP

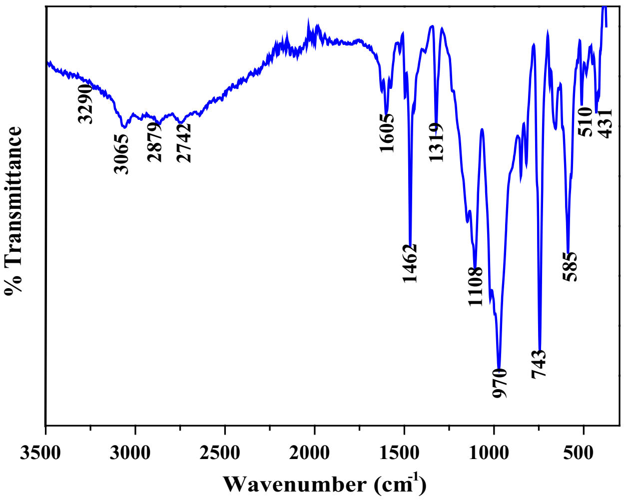


Fig. 2 FT–IR spectrum of VO(BBP)(H_2O)(SO_4)

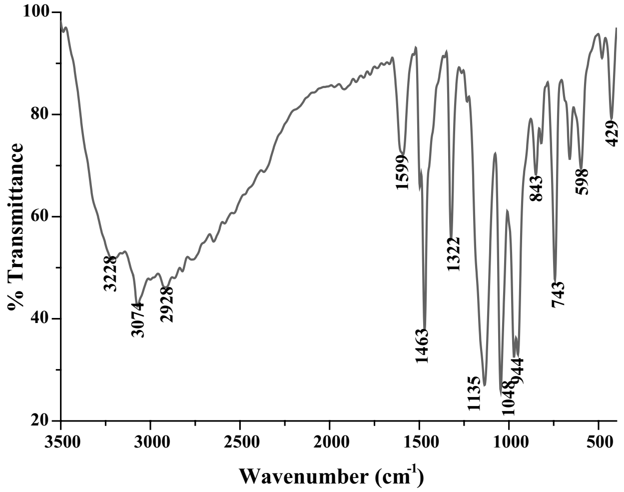


Fig. 3 IR spectrum of VO(PS–BBP)(H_2O)(SO_4)

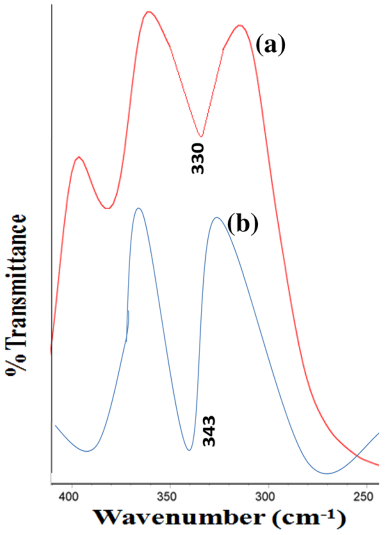


Fig. 4 Far IR spectra of (a) VO(PS–BBP)(H_2O)(SO_4) (b) VO(BBP)(H_2O)(SO_4)

and ν(N–H) at 1599 cm^{-1} and 3074 cm^{-1} respectively. The shift of ν(C=N) and ν(N–H) peaks in the supported complex when compared to PS–BBP, indicated the coordination of vanadium through N of C=N and N–H moieties of pyridine and benzimidazoles. The peaks at 1322 and 1463 cm^{-1} attributed to ν(C–N) and δ(N–H) respectively. The ν(V=O) peak was observed at 944 cm^{-1} and the peak due to sulphate group was at 1135 cm^{-1} (Fig. 3). The far-IR spectra of VO(PS–BBP)(H_2O)(SO_4) and VO(BBP)(H_2O)(SO_4) (Fig. 4) showed 330 and 343 cm^{-1} respectively due to ν(V–N).

3.1.3 Electronic Spectral Studies

The electronic spectra of both unsupported VO(BBP)(H_2O)(SO_4) and supported VO(PS–BBP)(H_2O)(SO_4) complexes exhibited strong absorption bands from 210 to 334 nm, which were attributed to π → π* and n → π* transitions of PS and BBP respectively, and another in the range 340 to 370 nm arising due to ligand to metal charge transfer band (LMCT) [33]. Spectra of both the complexes exhibited

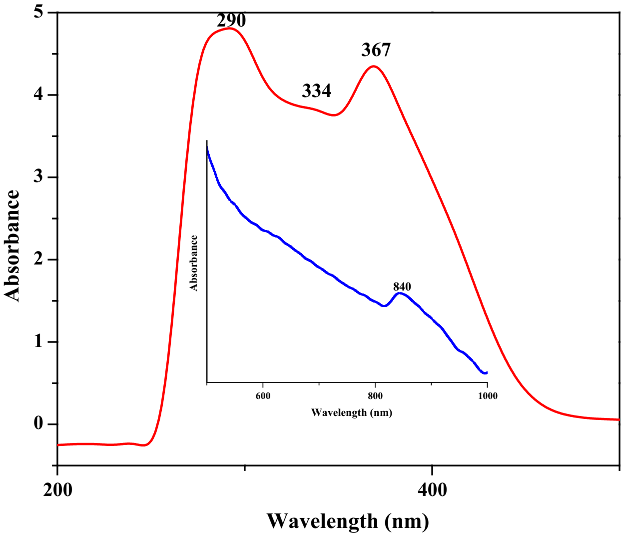


Fig. 5 Electronic spectrum of VO(BBP)(H_2O)(SO_4)

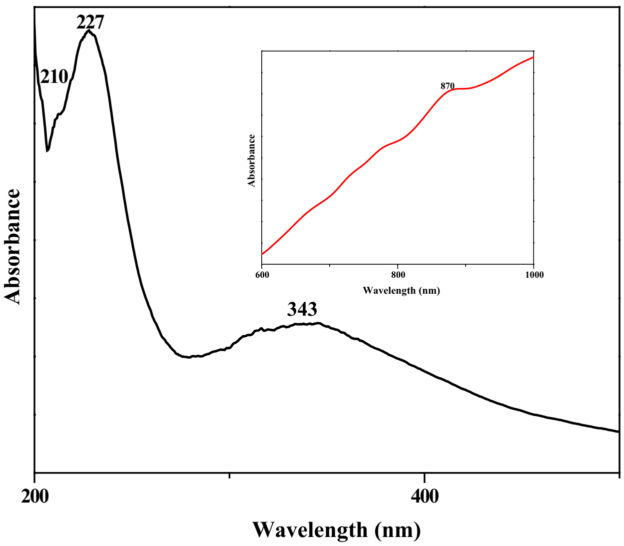


Fig. 6 Electronic spectrum of VO(PS–BBP)(H_2O)(SO_4)

two weak d–d bands in the visible region ~ 800–900 nm (dxy → dxz, dyz) and ~ 400–450 nm (dxy → dz^2), where latter is obscured under a strong CT band [36]. On the basis of electronic spectral data, an octahedral structure has been proposed for vanadium complexes (Figs. 5, 6).

3.1.4 ESR Spectral Studies and Magnetic Moment Measurements

The X-band room temperature ESR spectrum of VO(BBP)(H_2O)(SO_4) complex (Fig. 7) showed eight lines pattern, which is due to hyperfine splitting arising from the interaction of the unpaired electron with ^{51}V nucleus having nuclear spin of I = 7/2. This confirms the presence of a single vanadium(IV) cation as metallic center in the complex. The EPR spectrum of VO(PS–BBP)(H_2O)(SO_4) in polycrystalline state at RT (Fig. 8) exhibits an isotropic spectrum. The characteristic g_{iso} value obtained for both unsupported and supported complexes was 1.93, which is typical value of V(IV) complexes.

The room temperature magnetic moments of unsupported and polymer supported vanadium complexes were found to be 1.75 and 1.73 B.M respectively, indicating the presence of one unpaired electron (Table 1).

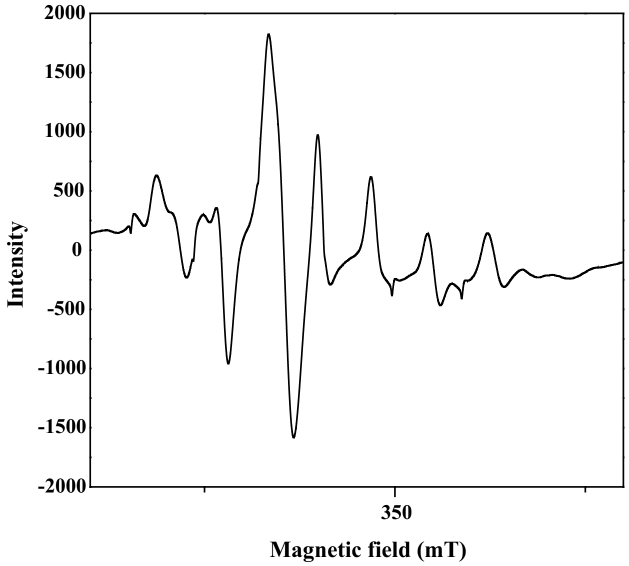


Fig. 7 EPR spectrum of VO(BBP)(H_2O)(SO_4) at RT

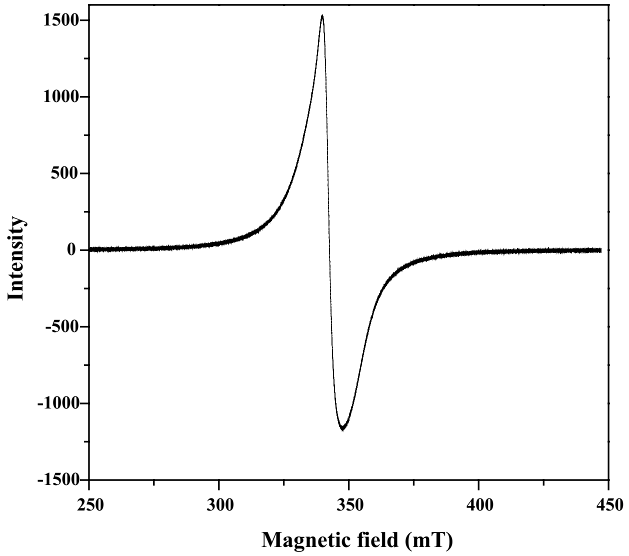
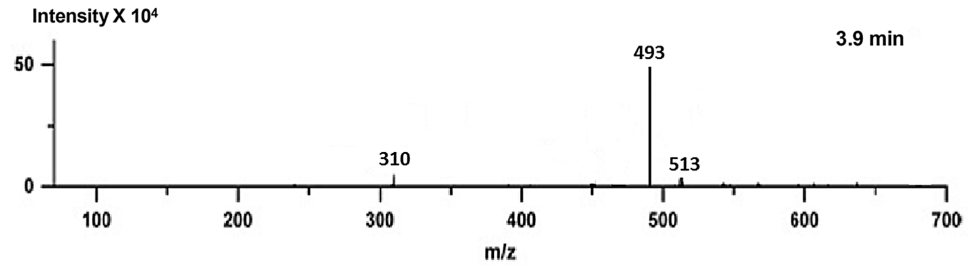


Fig. 8 EPR spectrum of VO(PS–BBP)(H_2O)(SO_4) at RT

Fig. 9 LC–MS of VO(BBP)(H_2O)(SO_4)



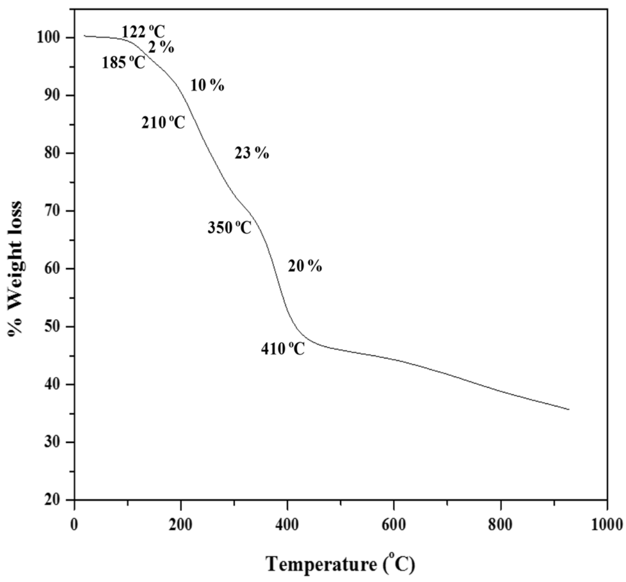


Fig. 10 Thermogram of VO(PS–BBP)(H_2O)(SO_4)

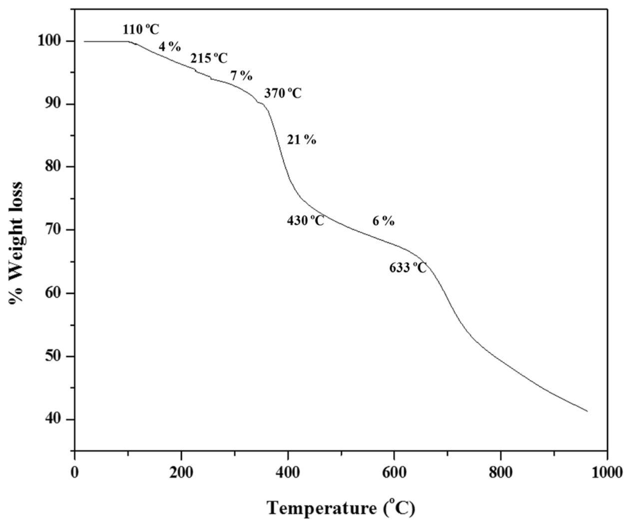


Fig. 11 Thermogram of VO(BBP)(H_2O)(SO_4)

3.1.5 LC–MS Studies

The molecular ion peak of complex VO(BBP)(H_2O)(SO_4) is observed at 493 m/z, which is in agreement with molecular formula $C_{19}H_{15}N_5O_6SV$. Further fragmentation of the complex revealed ion peak with m/z 310 due to BBP (Fig. 9).

3.1.6 Thermal Analyses

Thermograms of complexes were recorded in the range of 20–1000 °C at heating rate of 10 °C/min. The TG curve of VO(PS–BBP)(H_2O)(SO_4) (Fig. 10) indicated 2% first step weight loss at 122–185 °C due to water molecule. Second step involved weight loss of 10% at 185–210 °C attributable to the loss of sulphate ion. Third step weight loss (23%) at 210–350 °C was due to the loss of two benzimidazole moieties of BBP ligand. The loss of pyridine moiety of ligand and polymer occurred after 350 °C. The thermal decomposition of VO(BBP)(H_2O)(SO_4) showed weight loss of 4% due to loss of coordinated water molecule at 110–215 °C. The loss of sulphate ion (28%) took place at 215–430 °C. The decomposition of BBP occurred at higher temperature (> 430 °C) (Fig. 11).

All these studies revealed that polymer supported and unsupported V(IV) complexes were octahedral in geometry (Scheme 1a, b).

3.1.7 SEM and EDS Mapping Analysis

Surface of functionalized bead is smoother than that of complexed resin. The rough surface of the beads appeared because of the rearrangement of the polymer chains on complexation with metal ions.

A good dispersion of V(IV) complex particles on the polymer support was evidenced by SEM microscopy (Fig. 12). It was believed that this sustain the immobilization of the complexes by coordination interaction between the vanadium ion and the N atoms of the functionalized supports. The SEM images showed the change of polymer supported V(IV) complex morphology after immobilization. The morphology of recycled polymer vanadyl complex is almost similar to the fresh catalyst.

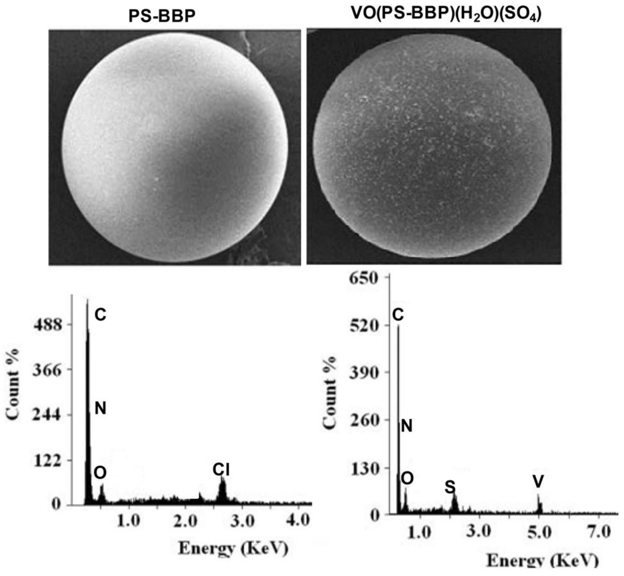


Fig. 12 SEM and EDS mapping analysis of PS–BBP and VO(PS–BBP)(H_2O)(SO_4)

3.2 Catalytic Activity: Benzyl Alcohol Oxidation

The BzOH oxidation was carried in absence of catalyst at 60 °C in 5 mL CH_3CN using O_2 as oxidant for 4 h, where conversion was only 15% (Fig. 13). When the reaction was carried out using supported (50 mg, 0.0995 mmol) and unsupported (48.96 mg, 0.0995 mmol) complexes of vanadium, the yield of benzaldehyde was 96% and 39% respectively. Since polymer supported catalyst showed higher conversion, it was used to optimize the reaction conditions.

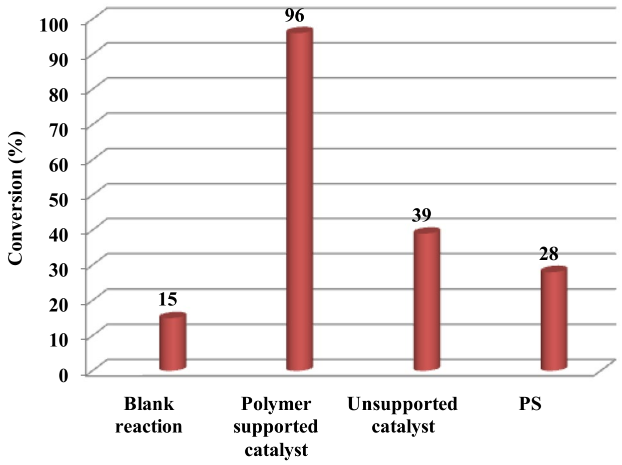


Fig. 13 Benzyl alcohol oxidation catalyzed by VO(BBP)(H_2O)(SO_4), VO(PS–BBP)(H_2O)(SO_4) and without catalyst (blank reaction)

3.2.1 Catalytic Activity of VO(PS–BBP)(H_2O)(SO_4)

To achieve the maximum conversion of BzOH, the parameters such as the oxidants, solvents, VO(PS–BBP)(H_2O)(SO_4) concentration and temperature were varied and their effect on the reaction was investigated. In all these reactions, it was observed that BzOH was converted to benzaldehyde with 100% selectivity.

3.2.2 Effect of Temperature and Time

The reactions were conducted at RT (30 °C) to 70 °C. The influence of reaction temperature on the catalytic activity of VO(PS–BBP)(H_2O)(SO_4) under reaction conditions is illustrated in Fig. 14. The BzOH conversion increased as the reaction proceeded from RT (59%) to 60 °C (96%). When the temperature increased from 60 to 70 °C BzOH conversion (85%) was decreased which is due to the decomposition of oxidant at higher temperature. Hence, for BzOH conversion, 60 °C for 4 h was considered as optimum.

3.2.3 Effect of Solvents

To investigate the influence of the solvent nature on the catalytic oxidation, the reaction was conducted in water, THF and acetonitrile. It was observed that the conversion followed the order: 96% in acetonitrile (dielectric constant $\varepsilon = 37.5$, donor number $D = 14.1$) > 72% in THF ($\varepsilon = 7.3$, $D = 20$) > 36% in H_2O ($\varepsilon = 80.4$, $D = 29.8$). Among them, acetonitrile was found to be the most suitable solvent for the reaction (Fig. 15).

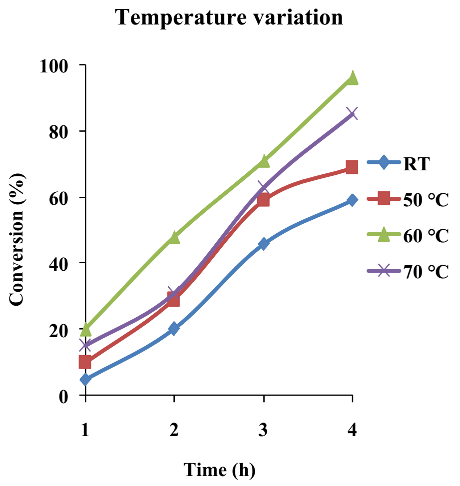


Fig. 14 Effect of temperature on the oxidation of BzOH, Reaction conditions: VO(PS–BBP)(H_2O)(SO_4) (50 mg), CH_3CN (5 mL); O_2 (1 atm)

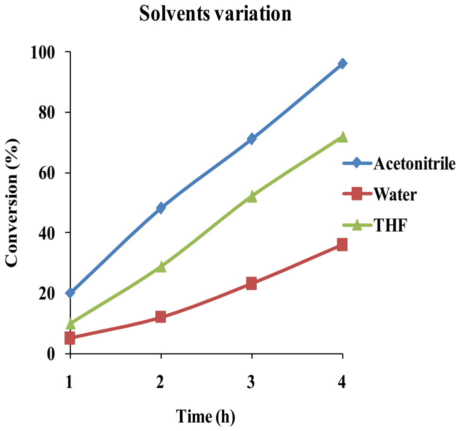


Fig. 15 Effect of solvents on the oxidation of BzOH, reaction conditions: VO(PS–BBP)(H_2O)(SO_4) (50 mg), solvent (5 mL); O_2 (1 atm); Temperature (60 °C) in 4 h

3.2.4 Effect of Catalyst Amount

Varying concentrations of VO(PS–BBP)(H_2O)(SO_4) catalyst (40, 50 and 60 mg), illustrates the conversion in the order 50 mg (0.0995 mmol, 96%) > 60 mg (0.1194 mmol, 72%) > 40 mg (0.0796 mmol, 62%) (Fig. 16). Hence, 50 mg VO(PS–BBP)(H_2O)(SO_4) is optimal concentration of the catalyst. The yield increases with increase in concentration up to certain extent, afterwards yield decreases due to the presence of excess of catalytic sites may results rapid decomposition of oxidant before oxidizing the substrate.

3.2.5 Effect of Oxidant

The effect of different oxidants on the oxidation of BzOH over VO(PS–BBP)(H_2O)(SO_4) catalyst at 60 °C in acetonitrile is depicted in Fig. 17. The BzOH conversion was found to be same (96%) in H_2O_2, TBHP and O_2, although the time taken for the conversion was 2, 3, and 4 h respectively. Though the time taken by O_2 was longer compared to H_2O_2 and TBHP, O_2 was chosen as oxidant since it is environmentally benign.

Using above optimized reaction conditions, activity and scope of catalyst was explored in the oxidation of primary and secondary benzyl alcohols (Table 2). Both electron rich (entries 1–4) and electron deficient (entries 5, 6) derivatives of BzOH showed excellent reactivity and afforded the corresponding aldehydes. The effect of substituents on the BzOH oxidation was studied and conversion was found in the order $NH_2 > OH > CH_3 > OCH_3 > NO_2$. Secondary alcohols, phenylethanol (70%) and phenylpropanol (68%) conversion was slightly lower (entries 7 and 8).

3.3 Comparison of Catalytic Activity with the Literature

The performance of VO(PS–BBP)(H_2O)(SO_4) is compared with literature work and it is tabulated in Table 3.

3.4 Catalyst Recyclability

Recycling study of the VO(PS–BBP)(H_2O)(SO_4) catalyst for the oxidation of BzOH under optimized reaction conditions was investigated (Fig. 18). After the first use, the supported catalyst was recovered by simple filtration and reused after washing and drying. The recovered catalyst was successfully employed in subsequent six cycles revealing excellent conversion and its activity decreased from seventh run (92%). Vanadium content of the recycled catalyst (after sixth cycle)

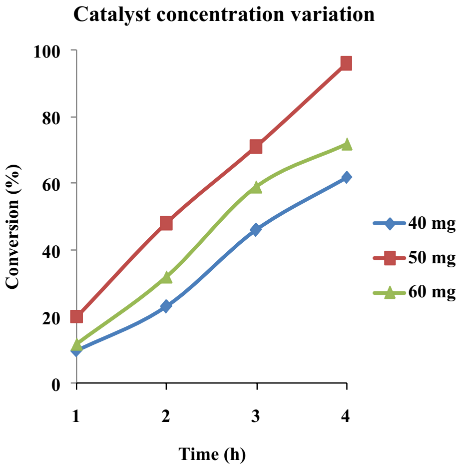


Fig. 16 Effect of VO(PS–BBP)(H_2O)(SO_4) concentration on the oxidation of BzOH, Reaction conditions: CH_3CN (5 mL); O_2 (1 atm); Temperature (60 °C) in 4 h

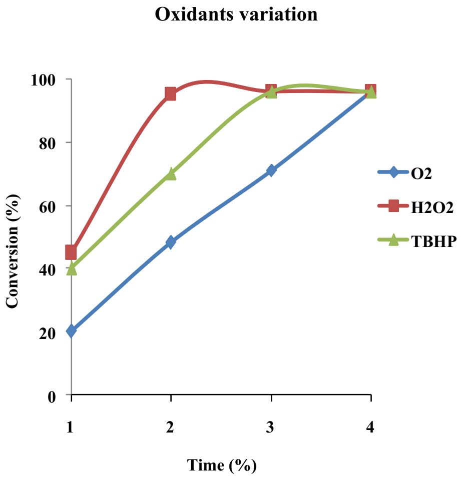
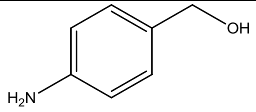
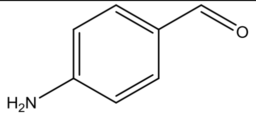
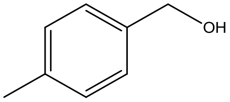
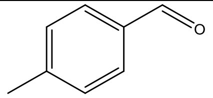
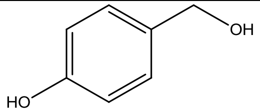
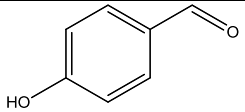
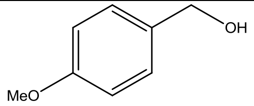
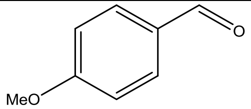
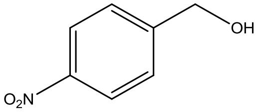
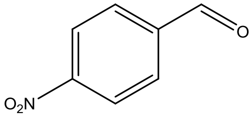
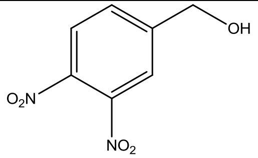
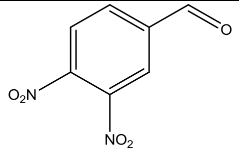
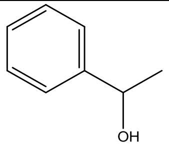
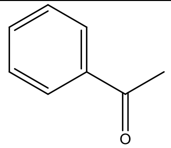
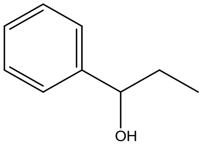
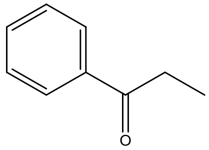


Fig. 17 Effect of oxidants on the oxidation of BzOH, reaction conditions: VO(PS–BBP)(H_2O)(SO_4) (50 mg), CH_3CN (5 mL); oxidants (H_2O_2 and TBHP; 30 mmol)/O_2 (1 atm); temperature (60 °C) in 4 h

Table 2 VO(PS–BBP)(H_2O)(SO_4) catalyzed oxidation of benzyl alcohol surrogates

Entry	Substituted benzyl alcohol	Aldehyde	% conversion	TON	TOF (h^{-1})
1			97	294	74
2			90	273	69
3			91	275	69
4			85	257	64
5			80	242	61
6			75	227	57
7			70	212	50
8			68	206	52

Reaction conditions: VO(PS–BBP)(H_2O)(SO_4) (50 mg), CH_3CN (5 mL); O_2 (1 atm); Temperature (60 °C) in 4 h

Table 3 Evaluation of present work with other reported catalysts

Catalyst	Catalyst conc.	Temp. (°C)	Oxidant	Time (h)	Yield	Selectivity	Refs.
Poly(S-DVB-EDTA-Cu)	150 mg	50	O_2	6	42	42	[37]
Poly(S-DVB-EDTA-Co)	50 mg	50	TBHP	2	50	100	[38]
Au/Ni_3Al HT	50 mg	50	O_2	24	74.5	> 99	[39]
Polymer supported Ru(III)salan complex	7.12×10^5 mol L^{-1}	35	O_2	1	Rate of reaction = 0.50 mL min^{-1}		[40]
PS–$(QBIM)_2$Cu(II) complex	0.02 mmol	50	TBHP	3	98	96	[41]
[PS–Cu–TSC] catalyst	50 mg	60	H_2O_2	6	100	100	[42]
([aqua(4-bromobenzoato) (2,2′dipyridylamine)copper(II)](perchlorate))	0.1 mol %	70	H_2O_2	6	71	100	[43]
Present work	50	60	O_2	4	96	100	–

[PS–Cu–TSC], polymer-supported thiosemicarbazone copper(II) complex; QBIM, 2-quinolylbenzimidazole

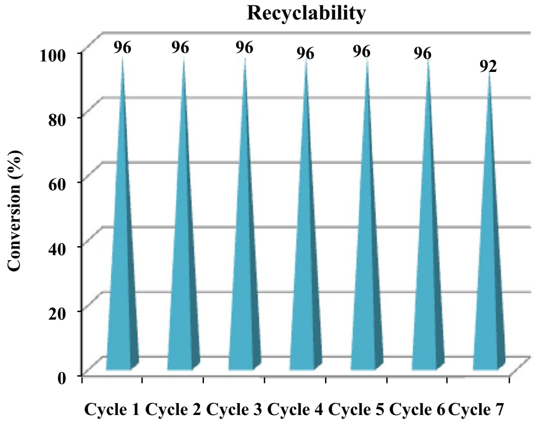


Fig. 18 Recycling ability of VO(PS–BBP)(H_2O)(SO_4)

was determined by ICP-OES and it is found that 5% (In Fresh catalyst, vanadium content is 5.6%). TGA of recycled catalyst is similar to the TGA of Fresh catalyst.

3.5 Heterogeneity Test

In order to see whether the present catalyst was functioning in truly heterogeneous manner, the conventional hot filtration test was carried out for oxidation reaction under optimized conditions. After 1 h, the catalyst was immediately filtered off from the hot reaction mixture. Vanadium content in the hot filtrate was determined by ICP-OES, and the absence of metal indicated that the reaction was truly heterogeneous in nature.

4 Conclusion

A highly efficient heterogeneous catalyst VO(PS–BBP)(H_2O)(SO_4) for oxidation of variety of benzyl alcohols was synthesized and characterized. The supported complex efficiently catalyzed the oxidation of BzOH in acetonitrile using molecular oxygen as oxidant with 100% selectivity. The conversion of BzOH in presence of $O_{2,}$ revealed maximum conversion of 96%. The catalyst was recyclable and stable up to six runs.

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Compliance with Ethical Standard

Conflict of interest The authors declare that they have no conflict of interest.

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