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# Aerobic oxidation and oxidative bromination in aqueous medium using polymer anchored oxovanadium complex



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# Introduction

The selective aerobic oxidation and oxidative bromination of organic compounds are useful and fundamental transformations in organic synthesis [1,2]. In recent years, there has been an increasing interest in developing environmental friendly greener processes which are also economically viable in industrial chemistry [3]. With environmental and economic concerns, heterogeneous catalysis reaction using molecular oxygen as an oxidant is developed as desired green process for selective oxidation of alcohol and oxidative bromination of various organic substrates [4–10].

Up to now, numerous expensive metal (*e.g.* palladium and ruthenium) catalyst and toxic organic solvents have been traditionally used to accomplish most of the aerobic oxidation of alcohols [11–13]. On other hand, conventional bromination reaction requires hazardous and toxic elemental bromine [14–16]. In order to overcome these problems, several safe systems for the aerobic oxidation and oxidative bromination have been developed. One is the use of inexpensive metal catalyst for the aerobic oxidation and

# ABSTRACT

Polymer anchored oxovanadium catalyst was synthesized and characterized. Its catalytic activity was evaluated for the oxidation of various primary and secondary alcohols with molecular oxygen under mild reaction conditions. This catalyst was also effective for the oxidative bromination reaction of organic substrates with 90–100% selectivity of mono substituted products with  $H_2O_2/KBr$  at room temperature. The above reactions require low temperature, short time period and most importantly all the above reactions occur in aqueous medium. The developed catalyst can be facilely recovered and reused six times without significant decrease in activity and selectivity.

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use of bromide ion as a bromide source instead of bromine for oxidative bromination [17-21].

We have chosen polymer anchored vanadium complex as the heterogeneous catalyst and water as the green solvent for the aerobic oxidation and oxidative bromination. Vanadium exists on the surface of the earth more abundantly than copper, palladium or ruthenium [22]. It plays an important role in aerobic oxidation and oxidative bromination processes. In addition, heterogeneous catalysts have some advantages compared to homogeneous catalyst. Metals supported on materials such as alumina [23], amorphous silicates [24], polymers [25], zeolites [26], and MCM-41 [27] are commonly in use in heterogeneous catalysis. Nowadays functionalized polystyrene anchored catalysts are used to carry out various catalytic organic transformations [28–31]. Among them chloromethylated polystyrene are widely used as polymer support. These polystyrene anchored metal complexes are inert and reusable catalysts for various organic reactions.

In the chemical processes, traditional organic solvents are used in large quantities, which have led to various environmental and health concerns. As part of green chemistry efforts, a variety of cleaner solvents have been used as replacements [32–35]. As an alternative solvent, water has been paid extraordinary attention. Apart from being a chemically interesting solvent, water provides a cheap alternative for organic solvents, making it environmentally



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and economically interesting as well. So, based on the above two concepts, we tried to synthesize a polymer anchored oxovanadium complex which catalyse the aerobic oxidation of primary and secondary alcohols and oxidative bromination of various aromatic amines, aldehydes in aqueous medium.

Herein we report the synthesis and characterization of a polymer anchored oxovanadium complex and illustrate its application for the aerobic oxidation and oxidative bromination reactions in aqueous medium using hydrogen peroxide as an oxidant.

# Experimental

# Materials and instruments

All the reagents used were chemically pure and were of analytical reagent grade. The solvents were dried and distilled before use following the standard procedures [36]. Chloromethylated polystyrene was supplied by Sigma-Aldrich chemicals Company, USA. Other reagents were obtained from Merck or Fluka. A Perkin-Elmer 2400C elemental analyzer was used to collect micro analytical data (C, H and N). Vanadium content of the sample was measured by Varian AA240 atomic absorption spectrophotometer (AAS). The FT-IR spectra of the samples were recorded on a Perkin-Elmer FT-IR 783 spectrophotometer using KBr pellets. Diffuse reflectance spectra (DRS) were registered on a Shimadzu UV/3101 PC spectrophotometer. Mettler Toledo TGA/SDTA 851 instrument was used for the thermogravimetric analysis (TGA). Morphology of functionalized polystyrene and complex was analysed using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility.

#### Synthesis of polymer anchored ligand PS-teta

Ligand was readily prepared in two steps. Firstly, chloromethylated polystyrene (PS–CH<sub>2</sub>Cl) was converted into PS–CHO according to literature [37]. Triethylenetetramine (teta) was reacted with PS–CHO (in1:2 M ratio) in methanol solvent at refluxing condition for 24 h to prepare the yellow Schiff base compound. The mixture was cooled to room temperature and then filtered. The residue was washed with ethanol and dried under vacuum (Yield = 60%).

#### Loading of metal ions on to the polymer anchored ligand PS-teta

The loading of metal ions on the polymeric support was carried out as follows: the polymer anchored ligand (1.00 g) was stirred for 24 h with 0.100 g of VO(acac)<sub>2</sub> in 20 mL of methanol under refluxing condition. At the end of this reaction the metal loaded polymer was



Scheme 1. Preparation of polymer anchored VO(IV) complex.

#### Table 1A

Chemical composition of polymer anchored ligand and oxovanadium complex.

Compound	Colour	C%	H%	Cl %	N%	Metal%
PS-teta	Yellowish	77.76	6.52	3.37	7.20	_
PS-teta—VO	Greenish	70.60	5.96	3.30	6.56	4.72

filtered, washed thoroughly with ethanol, dioxane and methanol to ensure the removal of any unreacted metal ions and dried in vacuum for 6 h at 90  $^{\circ}$ C (Yield = 80%).

# General procedure for aerobic oxidation reaction catalysed by PS-teta–VO

The aerobic oxidation reactions were carried out in a 50 mL stainless steel autoclave at different temperatures under vigorous stirring for a certain period of time. We examined the catalytic activity of vanadium complex using alcohol as the substrate and molecular oxygen as the primary oxidant. The oxidation of alcohol (5 mmol) was conducted under oxygen pressure (5.0 bar) at 60 °C for 5 h in the presence of vanadium complex (5 mg) in water (5 mL). After the reaction, the organic products were separated from the reaction mixture by extraction with dichloromethane (5 mL  $\times$  2). The combined organic portions were dried and concentrated. Product analysis was performed by Varian 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column.

General procedure for oxidative bromination reaction of organic substrates catalysed by PS-teta–VO

In a typical reaction, aqueous 30% H<sub>2</sub>O<sub>2</sub> (20 mmol) was added to the mixture of substrates (10 mmol) and KBr (20 mmol) taken in 10 mL of water. Catalyst (50 mg) and HClO<sub>4</sub> (5 mmol) were added to it and the reaction mixture was stirred at room temperature. An additional 15 mmol HClO<sub>4</sub> was added to the reaction mixture in three equal portions at 30 min intervals under continuous stirring. After specified time of the reaction, the catalyst was filtered and the solid was washed with ether. The combined filtrates were washed with saturated sodium bicarbonate solution and then shaken with ether in a separating funnel. The organic extract was dried over anhydrous sodium sulphate. The products were analysed by Varian 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a Flame Ionization Detector.

# **Results and discussion**

#### *Characterization of polymer anchored oxovanadium complex*

The reaction of aldehyde functionalised polystyrene and triethylenetetramine (teta) in methanol leads to the formation of polymer anchored Schiff base ligand. During this process CHO group of the polymer reacts with amine group of the triethylenetetramine (teta) moiety as shown in Scheme 1. The polymer anchored Schiff base ligand, on reaction with VO(acac)<sub>2</sub>, gave an oxovanadium(IV) complex which we designate as PS-teta–VO. The physicochemical data of the polymer anchored ligand and polymer

Table 1B	
Chemical composition of poly	mer supported oxovanadium complex.

Compound	Ligand loading (mmol equiv. g <sup>-1</sup> of resin)	Metal ion loading (mmol equiv. g <sup>-1</sup> of resin)	Ligand:metal
PS-teta-VO	1.17	0.93.	1.26:1

supported oxovanadium complex are presented in Table 1A. The loading of ligand and vanadium metal per gm of polymer is 1.17 mmol and 0.93 mmol, respectively. These data show that metal to ligand loading in polymer complex is close to 1:1 (Table 1B). Scheme 1 presents the proposed structure of the anchored

complex. Due to insolubilities of the polymer anchored oxovanadium(IV) complex in all common organic solvents, its structure has been established on the basis of elemental analyses, spectroscopic FT-IR and electronic studies, scanning electron micrographs (SEM) equipped with EDX facility and thermogravimetric analysis (TGA).



Fig. 1. FT-IR Spectra of polymer anchored ligand PS-teta (A) and PS-teta–VO complex (B).



Fig. 2. DRS-UV-visible absorption spectra of the polymer supported oxovanadium catalyst.

The attachment of metal onto the support was confirmed by comparison of the FT-IR spectra of the polymer before and after loading of metal (Fig. 1). The IR spectrum of pure chloromethylated polystyrene has an absorption band at 1261 cm<sup>-1</sup> due to the C-Cl group, which was weak in the ligand and in the catalyst. IR spectra show a stretching vibration for  $-CH_2$  at 2920 cm<sup>-1</sup> in the polymer bound ligand. The stretching vibration of C=N bond appeared at 1642 cm<sup>-1</sup> for the polymer-bound Schiff base ligand which is lowered to 1611 cm<sup>-1</sup> in the metal complex, indicating the coordination of azomethine nitrogen to the metal. A strong broad band around 3429 cm<sup>-1</sup> in polymeric ligand is observed due to NH (secondary amine) vibration which is lower to 3419 cm<sup>-1</sup> in metal complex. Polymer anchored oxovanadium complex showed two new bands at 546 and 463 cm<sup>-1</sup> assigned to v(V-O) and v(V-N), respectively [25]. Again a band appeared around 968 cm<sup>-1</sup> due to stretching vibration of V=0 [38].

The electronic spectrum of the polymer anchored metal complex has been recorded in diffuse reflectance spectrum mode as MgCO<sub>3</sub>/BaSO<sub>4</sub> disks (Fig. 2). In the UV spectrum of the catalyst, one absorption band is observed around 350-450 which may be assigned to the charge transfer transition. The band at around 580 nm is caused by d-d electronic transition of vanadium present in the complex [39]. Field emission-scanning electron micrographs of single bead of polymer anchored ligand (PS-teta) and its complex PS-teta–VO were recorded and it was observed that the morphological changes occurred on the polystyrene beads at various stages of the synthesis. The SEM images of polymer anchored ligand (A) and the immobilized vanadium complex (B) on functionalized polymer are shown in Fig. 3. The polymer anchored ligand has a slight roughening of the top layer of polymer beads. This roughening is relatively more in complex. Also the presence of vanadium metal can be further proved by energy dispersive spectroscopy analysis of X-rays (EDAX) (Fig. 4) which suggests the formation of metal complex with the polymer anchored ligand.

Thermal stability of the complex was investigated using TGA at a heating rate of 10 °C/min in air over a temperature range of 30–600 °C (Fig. 5). Polymer anchored ligand decomposed in the temperature range 370–390 °C. After complexation of vanadium on polymer anchored ligand, thermal stability of the immobilized complex improved. Polymer anchored oxovanadium complex decomposed at 420–440 °C. So from the thermal stability, it concludes that polymer anchored metal complex degraded at considerably higher temperature.

#### Catalytic activity

Since polymer anchored metal systems exhibit catalytic activity in a wide range of the industrially important processes and have been extensively studied, we have decided to investigate the catalytic activity of polymer anchored oxovanadium complex in the aerobic oxidation of primary and secondary alcohols. Also we have studied the oxidative bromination reaction with  $H_2O_2$  and molecular  $O_2$  as oxygen sources.

# Aerobic oxidation of primary and secondary alcohols catalysed by PS-teta–VO

To test the catalytic activity of the present catalyst, first aerobic oxidation of primary alcohols was tested in at 60 °C for 5 h. For optimization of reaction conditions, we choose the aerobic oxidation of benzyl alcohol as a probe reaction. In this case benzyl alcohol is selectively converted to benzaldehyde (Scheme 2).

Effects of various solvents on the conversion of benzyl alcohol and selectivity of benzaldehyde using polymer anchored VO(IV) catalyst are summarized in Table 2. We investigated the ability of various solvents like ACN, ethanol, toluene, DMSO and water (Table 2, entries 1–5). Selectivity of benzaldehyde is low in ethanol and DMSO as compared to the other solvents like ACN and toluene. It was observed that vanadium complex exhibited highest catalytic activity and selectivity towards the aerobic oxidation of benzyl



Fig. 3. FE-SEM images of polymer anchored ligand PS-teta (A) and PS-teta-VO complex.





Fig. 4. EDAX data of polymer supported ligand PS-teta (A) and PS-teta–VO complex (B).



**Fig. 5.** Thermogravimetric weight loss plots for the polymer supported ligand (a) (PS-teta) (b) PS-teta–VO complex.

alcohol in water (Table 2, Entry 7). Polymer anchored catalyst (3 mg) afforded a conversion of 64% within 5 h (Table 2, entry 5). No by-products such as benzoic acid were detected under this reaction condition. When the amount of the catalyst increased up to 4 mg, the conversion had an apparent increase and a 76% conversion was achieved but in this condition a little amount of benzoic acid was detected (Table 2, entry 6). A further increase in catalyst amount up to 5 mg led to an increase in the conversion of 92% (Table 2, entry 7). However, when the catalyst amount continuously increased up to 6 mg, the conversion remains almost constant but the selectivity of benzaldehyde reduces (Table 2, entry 8). These findings indicate that the oxidation of benzyl alcohol is highly dependent on the amount of the solid catalyst.

The conversion of benzyl alcohol is dependent on the amount of oxygen pressure applied. The effect of the amount of  $O_2$  on the



Scheme 2. Aerobic oxidation of various benzyl alcohols.

 Table 2

 Effect of solvent and catalyst amount on oxidation of benzyl alcohol using polymer anchored oxovanadium catalyst.

Entry	Solvent	Catalyst (mg)	Conversion (%)	Selectivity (%)	
				A	В
1	ACN	5	68	100	_
2	DMSO	5	73	92	08
3	EtOH	5	76	88	12
4	Toluene	5	81	100	_
5	H <sub>2</sub> O	3	64	100	_
6	H <sub>2</sub> O	4	76	97	03
7	$H_2O$	5	92	96	04
8	$H_2O$	6	92.3	86	14

Reaction conditions: benzyl alcohol (5 mmol), temperature (60  $^\circ\text{C})$ , time (5 h) and O2 (5 bar).

The bold values signifies optimized conditions.

oxidation of benzyl alcohol into benzaldehyde was studied and the results are shown in Table 3. The amount of pressure of molecular oxygen was varied from 2 bar to 6 bar (Table 3, entries 3 and 6–9), 2 bar oxygen pressure resulted in 58% conversion when the amount of catalyst was 5 mg and reaction time was 5 h at 60 °C temperature (Table 3, entry 6). When oxygen pressure was raised to 5 bar, the conversion increased to 92% at 60 °C (Table 3, entry 3). However, the conversion was found almost constant when oxygen pressure was further increased up to 6 bar (Table 3, entry 9). Therefore, 5 bar oxygen pressure were found to be optimum. The reaction shows very low conversion when molecular oxygen is absent (Table 3, entry 5). The influence of temperature on the aerobic oxidation of benzyl alcohol was investigated by performing the reaction at a temperature range from 40 to 70 °C (Table 3, entries 1–4) with all other parameters fixed. The results are given in Table 3 which reveals that the conversion is dependent on temperature and maximum conversion was recorded at 60 °C. Therefore, 60 °C was selected as the optimum temperature. At lower temperature, the conversion of benzyl alcohol into benzaldehyde was considerably decreased.

In order to study the further catalytic activity of the catalyst for the aerobic oxidation of aromatic alcohols, a series of benzyl alcohols bearing electron-withdrawing and electron donating groups was studied in water (Table 4). Substrates having both electron donating and electron withdrawing groups in the aromatic ring, 4methoxy and 4-nitro benzyl alcohols were oxidized to the corresponding aldehydes in high yields. On the other hand, various secondary alcohols could be oxidized by the use of PS-teta–VO catalyst. The general reaction is shown in Scheme 3 and the results are summarised in Table 5.

Initially, the oxidative bromination reaction of *p*-cresol (10 mmol) with PS-teta–VO (0.050 g), KBr (20 mmol) in 10 mL of water under molecular oxygen was investigated (Scheme 4) in presence of HClO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>.

#### Table 3

Effect of temperature and molecular oxygen on oxidation of benzyl alcohol using polymer anchored oxovanadium catalyst.

Entry	Temperature (°C)	O <sub>2</sub> pressure (bar)	Conversion (%)
1	40	5	68
2	50	5	76
3	60	5	92
4	70	5	92
5	60	-	12
6	60	2	58
7	60	3	77
8	60	4	84
9	60	6	92

Reaction conditions: benzyl alcohol (5 mmol), water (5 mL), catalyst (5 mg) and time (5 h).

Oxidative bromination reaction catalysed by PS-teta-VO

Two different parameters such as volume of HClO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> were varied at room temperature. The role of hydrogen peroxide was confirmed by conducting the oxidative bromination reaction using 10 mmol-20 mmol of  $H_2O_2$  (Table 6, entries 1-4) whereas in a blank experiment, in which H<sub>2</sub>O<sub>2</sub> was absent, the formation of bromo compound was significantly less (Table 6, entry 5). Conversion of *p*-cresol significantly improves from 65% to 94% with the increment of HClO<sub>4</sub> from 10 mmol to 20 mmol (Table 6, entries 3 and 4). 20 mmol of HClO<sub>4</sub> and 20 mmol of H<sub>2</sub>O<sub>2</sub> were found to be sufficient to give maximum conversion (Table 6, entry 4). The bromination reaction proceeded to allow the formation of the monobromide. This bromination was less effectively performed under argon atmosphere (Table 6, entry 6). Under the air atmosphere, the conversion of *p*-cresol was decreased slightly (Table 6, entry 9). In absence of HClO<sub>4</sub> under identical conditions showed a 48% yield (Table 6, entry 7). These results indicate that the presence of the acid is essential for the efficient catalytic bromination. The presence of excess acid may decompose the catalyst under the above reaction conditions. HClO<sub>4</sub> was added to the reaction mixture in definite time interval to prevent decomposition of catalyst. Approximately 94% conversion of p-cresol with PS-teta-VO and 100% selectivity towards the formation of 2-bromo-p-cresol was observed. In the initial stage of the reaction, 2-bromo-p-cresol was selectively produce, if the reaction was carried out for longer time (Table 6, entry 8) after consumption of the unreacted substrates, the formation of 2,6-dibromo-p-cresol was started. With increase of temperature the conversion of *p*-cresol was almost same. The amount of KBr was also varied from 5 mmol to 20 mmol and the maximum conversion of p-cresol was observed using 20 mmol of KBr (Table 6, entries 1-4).

Oxidative bromination reaction of other organic substrates has been studied under optimized reaction conditions and the results are shown in Table 7. In the present bromination system, simple aromatic compound such as anisole was subjected to the monobromination (Entry 2). Additionally, the phenol derivative bearing the electron-withdrawing group was brominated smoothly to the monobromide. 4-nitrophenol was also converted to the *o*-bromination product of 82% yield (Entry 4), whereas the bromination of 2-formylphenol resulted in the formation of 4-bromo-2formylphenol (Entry 1). Similarly, substrates like resorcinol, aniline and *N*,*N*-dimethylaniline showed high conversion and excellent *para*-selectivity (Entries 3, 5 and 6).

# Comparison with other reported system

Oxidation of primary, secondary alcohols and oxidative bromination of various aromatic substrates under heterogeneous conditions over a variety of catalysts has been studied (Table 8). Table 8 provides a comparison of the results obtained for our present catalytic system with those reported in the literature [1,3,6,40–42]. From Table 8, it can be concluded that the present catalyst follows a green pathway and shows excellent catalytic activities as compared to other reported systems [1,3,6,40–42]. Reactions conducted at low or room temperature, shorter reaction time was required for these reactions and most importantly most of the coupling reactions occurred in water using our vanadium catalyst.

#### Test for heterogeneity

The leaching of vanadium from polymer anchored VO complex was confirmed by analysis of the used catalyst (FTIR) as well as the product mixtures (AAS and UV–Vis). Analysis of the used catalyst did not show appreciable loss in the vanadium content as compared to the fresh catalyst. IR spectrum of the recycled catalyst

#### Table 4

Entry	Substrate	Product	Conversion (%) <sup>a</sup>	TON
1	ОН	CHO	92	993.5
2	ОН	СНО	93	1004.3
3	ОН	CHO	94	1015.1
4	ОН	CHO	88	950.3
5	МеО	MeO	96	1036.7
6	СІ	CI	81	874.7
7	Br	Br	79	853.1
8	OH	CHO	77	831.5
9	O2N OH	O <sub>2</sub> N CHO	78	842.3
10	OH NO <sub>2</sub>	CHO NO <sub>2</sub>	84	907.1
11	F <sub>3</sub> C OH	F <sub>3</sub> C CHO	75	809.9
12	H3COC OH	H3COC	74	799.1

Reaction condition: Substrate (5 mmol), water (5 mL), catalyst (5 mg), O\_2 (5 bar), time (5 h) at 60  $^\circ\text{C}.$ 

<sup>a</sup> Determined by GC.

was quite similar to that of fresh sample indicating the heterogeneous nature of this complex. Analysis of the product mixtures showed that if any vanadium was present it was below the detection limit. The UV–vis spectroscopy was also used to determine the stability of this catalyst. The UV–vis spectra of the reaction solution, at the first run, did not show any absorption peaks characteristic of vanadium metal, which indicates that the leaching of metal did not take place during the course of the reaction. The metal content of the recycled catalyst was determined with the help of AAS and it was found that vanadium content of the recycled catalyst remained almost unaltered. These observations strongly suggest that the present catalyst is truly heterogeneous in nature.



Scheme 3. Aerobic oxidation of secondary alcohols.

Table 5 Polymer supported oxovanadium complex catalysed aerobic oxidation of secondary alcohols.

Entry	R	х	Time (h)	Conversion (%) <sup>a</sup>	TON
1	CH <sub>3</sub>	Н	5	95	1025.9
2	CH <sub>3</sub>	CH <sub>3</sub>	5	90	971.9
3	CH <sub>3</sub>	OMe	5	88	950.3
4	$CH_3$	Br	5	92	993.5
5	Ph	Н	6	97	1047.5
6	Ph	Cl	6	98	1058.3
7	<sup>i</sup> Pr	Н	6	99	1069.1

Reaction condition: Substrate (5 mmol), water (5 mL), catalyst (5 mg), O<sub>2</sub> (5 bar), at 60 °C. <sup>a</sup> Determined by GC.



Scheme 4. Oxidative bromination of *p*-cresol in water.

Heterogeneity test was carried out for the oxidation of benzyl alcohol as an example. For the rigorous proof of heterogeneity, a test was carried out by filtering catalyst from the reaction mixture at 60 °C temperature at 2 h and the filtrate was allowed to react up to the completion of the reaction (5 h). The reaction mixture of 2 h

#### Table 6

Effect of KBr, HClO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> on oxidative bromination of *p*-cresol.

Entry I	KBr	HClO <sub>4</sub>	$H_2O_2$	Conversion <sup>a</sup>	Product selectivity (%)	
	(mmol)	(mmol)	(mmol)	(%)	Monobromo	Dibromo
1	05	10	10	37.0	100	_
2	10	10	15	54.0	100	_
3	20	10	20	65.0	100	_
4	20	20	20	94.0	100	_
5	20	20	_	25.0	100	_
6 <sup>b</sup>	20	20	20	79.0	100	_
7 <sup>c</sup>	20	_	20	48.0	100	_
8 <sup>d</sup>	20	20	20	94.3	95	05
9 <sup>e</sup>	20	20	20	91	100	

Reaction conditions: substrate (10 mmol), water (10 mL), 5 mg catalyst at room temperature under oxygen atmosphere.

The bold values signifies optimized conditions.

<sup>a</sup> Determined by GC.

<sup>b</sup> Under argon atmosphere.

<sup>c</sup> Absence of acid.

<sup>d</sup> Longer reaction time.

<sup>e</sup> Under air atmosphere.

#### Table 7

Oxidative bromination of various organic substrates catalysed by polymer anchored VO(IV) catalyst.



Reaction conditions: substrate (10 mmol); HClO<sub>4</sub> (20 mmol); 30% aq. H<sub>2</sub>O<sub>2</sub> (20 mmol), water (10 mL), 5 mg catalyst at room temperature, under oxygen atmosphere.

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Comparison of catalytic activities of the present catalyst in the oxidation and oxidative bromination reactions with other reported systems.

Reaction	Catalyst	Reaction conditions	Conversion (%)	TON	Ref.
Oxidation of alcohol	(VO) <sub>4</sub> (hpic) <sub>4</sub>	O <sub>2</sub> (1 MPa), 120 °C, CH <sub>3</sub> CN	62 <sup>a</sup>	186	[1]
	PS-[VO-An]	30% H <sub>2</sub> O <sub>2</sub> , 50 °C, water	96 <sup>a</sup>	74.4	[3]
	Pani–VO(acac) <sub>2</sub>	O <sub>2</sub> (1 atm), 100 °C, toluene	98 <sup>a</sup>	42.61	[6]
			95 <sup>b</sup>	41.30	
	[bmim]BF <sub>4</sub> -VO(acac) <sub>2</sub>	O <sub>2</sub> (1 atm), 80 °C, ionic liquid, Et <sub>3</sub> N	91 <sup>b</sup>	18.2	[40]
	PS-teta-VO	O <sub>2</sub> , 60 °C, water	92 <sup>a</sup>	993.5 <sup>c</sup>	This work
			96 <sup>b</sup>	1036.7 <sup>d</sup>	
Oxidative bromination of	PS-im [VO <sub>2</sub> (pan)]	H <sub>2</sub> O <sub>2</sub> , 40 °C, water	96	2254 (TOF)	[41]
salicylaldehyde	PS-[VO-An]	$H_2O_2$ , RT, water	98	75.97	[3]
	PS-K	$H_2O_2$ , RT, water	85.2	775 (TOF)	[42]
	[VO <sub>2</sub> (salinh)(im)]				
	PS-teta-VO	H <sub>2</sub> O <sub>2</sub> , RT, water	98	2116.6	This work

<sup>a</sup> Oxidation of benzyl alcohol.

<sup>b</sup> Oxidation of p-methoxy benzyl alcohol.

and the filtrate were analysed by gas chromatography. No change in the conversion as well as selectivity was found which indicates that the present catalyst was heterogeneous in nature.

#### **Recycling of catalyst**

The catalyst remains insoluble in the present reaction conditions and hence can be easily separated by simple filtration followed by washing. The catalyst was washed with dichloromethane and dried at 100 °C. Oxidation of benzyl alcohol was carried out with the recycled catalyst under the optimized reaction conditions. The catalyst was recycled in order to test its activity as well as stability. The obtained results are presented in Fig. 6. As seen from Fig. 6, the recycled catalyst did not show any appreciable change in the activity which indicates that the catalyst is stable and can be regenerated for repeated use. Similarly, recycling of the catalyst was tested for the oxidative bromination reaction of *p*-cresol. No appreciable change in conversion as well as selectivity indicates that the catalyst can be reused.

# Conclusion

In the present work, we have developed and characterized an efficient polymer anchored oxovanadium Schiff base complex as



**Fig. 6.** Recycling efficiency for the aerobic oxidation of benzyl alcohol and oxidative bromination of *p*-cresol with PS-teta–VO complex.

the catalyst for the selective aerobic oxidation of primary and secondary alcohols to the corresponding carbonyl compounds via ideal green process, i.e. water as the green solvent and with molecular oxygen as oxidant. This catalyst also shows excellent catalytic activity in oxidative bromination reaction in water at room temperature. Another important factor is the stability and recyclability of the catalyst under the reaction conditions used. This heterogeneous catalyst shows no significant loss of activity in the recycling experiments. The active sites do not leach out from the support and thus can be reused without appreciable loss of activity, indicating that the anchoring procedure was effective. The reusability of this catalyst is high and can be reused six times without significant decrease in its initial activity. We hope that the present catalytic system has a bright future in industrial application.

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