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Synthesis, characterization, and catalytic oxidation of styrene, cyclohexene, allylbenzene, and *cis*-cyclooctene by recyclable polymer-grafted Schiff base complexes of vanadium(IV)

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ABSTRACT

Schiff base-functionalized chloromethylated polystyrenes, PS-[Ae-Eol] (I), PS-[Hy-Eda] (II) and PS-[HyP-Eda] (III), were synthesized by reacting 2-(2-aminoethoxy)ethanol (Ae-Eol), N-(2-hydroxyethyl) ethylenediamine (Hy-Eda), and N-(2-hydroxpropyl)ethylenediamine (HyP-Eda) with oxidized chloromethylated polystyrene. Oxidized chloromethylated polystyrene (PS-CHO) was prepared by oxidation of chloromethylated polystyrene (PS) with sodium bicarbonate in DMSO. By reacting DMSO solution of [VO(acac),] with polymeranchored Schiff base ligands I, II, and III, vanadium(IV) complexes PS-[V^{IV}O(Ae-Eol)] (1), PS-[V^{IV}O(Hy-Eda)] (2), and PS-[V^{IV}O(HyP-Eda)] (3) were prepared. Structure and bonding of I, II, and III as well as corresponding vanadium complexes 1, 2, and 3 were confirmed by FT-IR, UV-vis spectroscopy, SEM, EDX, AAS, TGA, EPR, etc. Polymeranchored vanadium(IV) complexes 1, 2, and 3 show, efficient catalysis toward oxidation of styrene, cyclohexene, allylbenzene, and cis-cyclooctene in the presence of hydrogen peroxide. Optimized reaction conditions for the oxidation of these alkenes was achieved by changing various reaction parameters (like amount of catalyst, amount of oxidizing agent, volume of solvent, etc.). Polymer-grafted 1, 2, and 3 can be reused multiple times without depletion of their activity.



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1. Introduction

In synthetic organic chemistry, catalytic oxidation products of alkenes such as carbonyl compounds, epoxides, and diols are the major feedstock among the most effective synthetic intermediates in fundamental research as well as industrial commodities [1–4]. Particularly oxidation of cyclohexene, styrene, cis-cyclooctene, allylbenzene, etc. produces versatile and useful intermediates widely used in polymers, pharmaceuticals, fine chemicals, and biological materials [5–8]. Certain herbs and spices, like basil, cinnamon, nutmeg, ginger, black pepper, clove, tarragon, etc. carry naturally occurring allylbenzenes (such as eugenol, estragole, and safrole) in high concentration, which can be a promising green alternative source of renewable raw materials for chemical industry. Oxidation products of allylbenzenes are widely used in pharmacological, cosmetic, food, and fragrance industries [9–12] as well as direct synthetic intermediates in the production of biologically active compounds [13]. 2-Cyclohexene-1-ol and 2-cyclohexene-1-one formed through the allylic oxidation of cyclohexene are applied in the manufacture of spices, medication, pesticides, and insect pheromones [14, 15]. Oxidation of styrene is one of the most important research tasks for converting hydrocarbons into other valuable commodities such as benzaldehyde, styrene epoxide, and formaldehyde [16–20]. Styrene oxide is widely used for the synthesis of epoxy resin-diluting agents, ultraviolet absorbents, flavoring agents, etc.; benzaldehyde is a precious chemical mainly used in perfumery, pharmaceuticals, dyestuffs, and agrochemicals [21]. Likewise, the oxidation products of cyclooctene have widespread applications in industrially important pharmaceuticals and fine chemicals [22]. Conventionally, stoichiometric amount of oxidants such as permanganates, chromium reagents, ruthenium(VIII) oxide or activated DMSO were used to carry out the oxidation of alkenes. From the last few decades, metal complexes of Ti, V, Cr, Mn, Co, Ni, Cu, Mo, Ru, and Re were utilized for oxidation of alkenes in the presence of peroxides, peracids, and other oxidizing reagents [4, 23-30]. Vanadium complexes in high oxidation states have been widely used as effective catalysts in oxidation reactions of industrial as well as academic interest in the presence of a suitable oxidant [26, 30-34]. Moreover, the involvement of vanadium haloperoxidase, a vanadium-containing enzyme in a variety of biological processes, stimulated the application of vanadium-containing enzymes in various catalytic organic transformations [1–4, 23–38]. Flexible coordination number, easily interconvertible high oxidation states between +4 and +5, Lewis acidic nature of the vanadium center along with high affinity toward oxygen make high valent vanadium complexes promising agents for the catalytic oxidation of alkenes.

Some drawbacks associated with the utilization of homogeneous catalysts need to be addressed, such as use of over stoichiometric ratio of costly oxidizing agents, stability of the catalysts, easy separation from the reaction mixture, recyclability as well as leaching of the metal during the reaction. In general, irreversible conversion of monomeric species into dimeric and polymeric species during the catalytic cycle along with difficulties in recovering and recycling of homogeneous catalysts discourages its application in industrial chemistry [39].

Covalent attachment of homogeneous catalysts on the surface of solid support allows easy catalyst separation, recyclability, and thermal stability and it can be considered as an effective strategy to make green and sustainable catalytic processes [40]. Furthermore, anchoring the homogeneous catalysts into the solid supports can effectively enhance reactivity of the catalysts as well as TOF of the catalytic reaction [41].

Among various inorganic, organic, and hybrid solid supports, chloromethylated polystyrene cross-linked with divinylbenzene-anchored heterogeneous catalysts emerged as an important research area in the field of catalytic oxidation of various organic substrates. Major advantages of using chloromethylated polystyrene as a solid support are easy availability, low price, higher thermal stability, and easy functionalization. In this connection, we have described herein an easy synthesis for polymer-anchored vanadium(IV) complexes of 2-(2-aminoethoxy)ethanol, N-(2-hydroxyethyl)ethylenediamine, and N-(2-hydroxpropyl) ethylenediamine. Interestingly, reaction of oxidize chloromethylated polystyrene (PS-CHO) with 2-(2-aminoethoxy)ethanol, N-(2-hydroxyethyl)ethylenediamine, and N-(2-hydroxpropyl) ethylenediamine produces polymer-anchored monobasic tridentate Schiff base ligands with OON and ONN donors. Polymer-anchored vanadium(IV) complexes efficiently oxidized a wide variety of alkenes under moderate reaction condition in a short reaction time. Use of a readily available, cheap, and environmentally green oxidizing agent like hydrogen peroxide makes the catalytic oxidation of alkenes more acceptable for academic and industrial purposes. Catalytic oxidation of alkenes by polymer-anchored vanadium complexes is available in the literature [38, 42–46]. However, uncomplicated and straightforward synthesis of polymer-anchored vanadium(IV) Schiff base complexes along with effective catalytic efficiency toward a wide range of alkenes makes the current polymer-anchored vanadium complexes labor-saving, cost-effective, energy-saving, and ecofriendly catalysts for catalytic oxidation of alkenes.

2. Experimental

2.1. Materials

Merrifield's peptide resin (1% cross-linked with divinyl benzene, 2.5–4.0 mmol/g Cl⁻¹ loading, Sigma–Aldrich, USA), 2-(2-aminoethoxy)ethanol 98% (Alfa Aeser, Great Britain), 2-(2-aminoethylamino)ethanol 99% (Sigma–Aldrich, USA), 1-(2-aminoethylamino)propan-2-ol 96% (TCl Chemicals, Japan), styrene 99% (Alfa Aeser, Great Britain), cyclohexene 99% (Alfa Aeser, Great Britain), allylbenzene 98% (Alfa Aeser, Great Britain), *cis*-cyclooctene 95% (Alfa Aeser, Great Britain), V₂O₅ (Loba Chemie, India), acetylacetone (SRL, India), Nujol (paraffin wax heavy liquid, SRL, India), and 30% H₂O₂ (Merck Chemicals, India) were used as received. All other solvents and reagents were of AR grade. HPLC grade solvents were used in the GC analysis. [V^{IV}O(acac)₃] was prepared as described [47].

2.2. Physical method and analysis

FT-IR spectra were recorded by ATR mode on an Agilent 600 series FT-IR spectrophotometer. Electronic spectra of the polymer-anchored metal complexes were recorded in Nujol on a SHIMADZU UV-1800 spectrophotometer. Surface morphology and elemental composition of polymer-supported compounds were analyzed by SEM and EDX on a HITACHI S-3400N instrument after coating the polymer surface with thin film of gold to block the surface charging and thermal damage by the electron beam. Percentage of metal loading into the polymeric matrix was confirmed by LABINDIA AA 8000 Atomic Absorption Spectrophotometer. Solid-state EPR spectra of the polymer-anchored metal complexes were recorded on a Bruker EMX X-band spectrometer operating at 100-kHz field modulation at room temperature.

Agilent 7890-Bgas chromatograph fitted with HP-5 capillary column ($30 \text{ m} \times 0.32 \mu \text{m} \times 0.25 \mu \text{m}$) and FID detector was used to analyze the reaction products. Percent conversion was calculated using calibrated plot. Identities of the reaction products were confirmed by a thermo ISQ QD single quadrupole mass analyzer coupled with a Trace 1300 GC system.

2.3. Preparations

2.3.1. Preparation of oxidized chloromethylated polystyrene

Oxidized chloromethylated polystyrene was prepared by following the reported procedure [48] (Scheme 1). Chloromethylated polystyrene beads (2.5 g, 1% cross-linked with divinyl benzene, 2.5–4.0 mmol/g Cl⁻¹ loading, and 50–100 mesh) were allowed to swell in DMSO (25 mL) for 12 h. A solution of sodium bicarbonate (1.125 g) was added to the above suspension and the reaction mixture was heated at 155 °C for 6 h with stirring. After cooling the reaction mixture to room temperature, oxidized chloromethylated polystyrene beads were filtered, washed with DMSO, followed by hot methanol and dried in an oven at 120 °C for 24 h. Presence of 1700 cm⁻¹ IR stretching band in the oxidized chloromethylated polystyrene proves the oxidation of chloromethylated polystyrene (PS) to the oxidized chloromethylated polystyrene (PS-CHO).

2.3.2. Preparation of PS-[Ae-Eol] (I), PS-[Hy-Eda] (II) and PS-[HyP-Eda] (III)

PS-[Ae-Eol] (I), PS-[Hy-Eda] (II), and PS-[HyP-Eda] (III) were prepared by following the method described in Scheme 1. In DMSO, oxidized chloromethylated polystyrene (0.500 g) was reacted with 2-(2-aminoethoxy)ethanol (Ae-Eol), N-(2-hydroxyethyl)ethylenediamine (Hy-Eda) and N-(2-hydroxpropyl)ethylenediamine (HyP-Eda) (1.0 g each), respectively, at 130 °C for 6 h. Then, dark polymer-bound compounds PS-[Ae-Eol] (I), PS-[Hy-Eda] (II), and PS-[HyP-Eda] (III) were filtered and washed with hot DMSO followed by hot methanol to remove unreacted and surface adsorbed (Ae-Eol), (Hy-Eda), and (HyP-Eda). The polymer beads were dried in an oven at 120 °C for 24 h.

2.3.2.1. Data of PS-[Ae-Eol] (I). Recovery yield 95%; FT-IR Stretching frequency (ATR mode, cm^{-1}): 1643($v_{C=0}$), 1601($v_{C=N}$), 3395(v_{O-H}).



Scheme 1. Proposed reaction methodology for the preparation of polymer-anchored ligands and metal complexes.

2.3.2.2. Data of PS-[Hy-Eda] (II). Recovery yield 96%; FT-IR Stretching frequency (ATR mode, cm^{-1}): 1649($v_{c=0}$), 1602($v_{c=N}$), 3358(v_{O-H}).

2.3.2.3. Data of PS-[HyP-Eda] (III). Recovery yield 95%; FT-IR Stretching frequency (ATR mode, cm⁻¹): $1652(v_{C=0})$, $1602(v_{C=N})$, $3373(v_{O-H})$.

2.3.3. Preparation of PS-[V^{IV}O(Ae-Eol)] (1), PS-[V^{IV}O(Hy-Eda)] (2) and PS-[V^{IV}O(HyP-Eda)] (3)

A DMSO solution (15 mL) of $[V^{IV}O(acac)_2]$ (7.54 mmol, 2.0 g) was mixed with pre-swelled (12 h in 15 mL DMSO) PS-[Ae-Eol] (I), PS-[Hy-Eda] (II), and PS-[HyP-Eda] (III), respectively, and allowed to heat at 130 °C for 72 h with slow and smooth stirring. Then, dark metal complex-bound polymer beads were filtered and washed with hot DMSO followed by hot methanol and dried in an oven at 120 °C for 24 h.

2.3.3.1. Data of PS-[V^{IV}O(Ae-Eol)] (1)

Recovery yield: 98%; FT-IR Stretching frequency (ATR mode, cm⁻¹): $1632(v_{C=0})$, $1604(v_{C=N})$, $3298(v_{O=H})$, $964(v_{V=O})$. UV–vis (Nujol, nm): 851, 756, 539, 362, 326.

2.3.3.2. Data of PS-[V^{IV}O(Hy-Eda)] (2)

Recovery yield: 97%; FT-IR Stretching frequency (ATR mode, cm⁻¹): 1636($v_{C=0}$), 1586($v_{C=N}$), 3234(v_{O-H}), 940($v_{V=0}$). UV-vis (Nujol, nm): 969, 766, 691, 551, 354, 297.

2.3.3.3. Data of PS-[V^{IV}O(HyP-Eda)] (3)

Recovery yield: 97%; FT-IR Stretching frequency (ATR mode, cm⁻¹): $1630(v_{C=0})$, $1603(v_{C=N})$, $3342(v_{O-H})$, $929(v_{V=0})$. UV-vis (Nujol, nm): 882, 528, 377, 337, 290.

2.4. Catalytic activity

Polymer-bound **1–3** were used as catalysts for oxidation of styrene, cyclohexene, allylbenzene, and *cis*-cyclooctene. For the best catalytic performance, optimized reaction conditions were achieved by changing the various reaction parameters such as catalyst amount, oxidant amount, solvent amount, and nature of solvent while taking styrene as the representative alkene. In a typical reaction, 10-mL methanolic solution of styrene (0.52 g, 5 mmol) was reacted with dilute aqueous solution of 30% H_2O_2 (1.14 g, 10 mmol) in the presence of preswelled catalysts **1–3** (0.015 g) at 70 °C for 6 h. Catalysts were swelled in methanol for 12 h before using in oxidation reactions. In a fixed time interval, a small portion of reaction mixture was withdrawn and analyzed in a gas chromatograph fitted with a HP-5 capillary column and a FID detector. Percent conversion was estimated using a calibration plot. Catalytic oxidation of cyclohexene, allylbenzene, and *cis*-cyclooctene under optimized reaction conditions was also examined and analyzed through GC periodically. Identities of the reaction products were established by GC-MS analysis using a thermo ISQ QD single quadrupole mass analyzer system equipped with a TG-5MS column (30 m × 0.32 µm × 0.25 µm); percent conversions of the substrates were calculated using the following equation.

% Conversion of substrate = $100 - \frac{\text{Area of substrate}}{\text{Total area of substrate} + \text{Area of products}} \times 100$

3. Results and discussion

3.1. FT-IR and UV-vis spectral analysis

Selected FT-IR data of polymer-anchored Schiff base ligands PS-[Ae-EoI] (I), PS-[Hy-Eda] (II), and PS-[HyP-Eda] (III) along with their corresponding vanadium complexes PS-[V^{IV}O(Ae-EoI)] (1), PS-[V^{IV}O(Hy-Eda)] (2), and PS-[V^{IV}O(HyP-Eda)] (3) are listed in Table 1. Due to poor loading of the metal complexes into the polymeric chain, intensity of the FT-IR spectrum is relatively weak, as displayed in Figures S1–S6. Oxidized polymer-anchored complexes show $v_{C=O}$ stretching frequency at 1700 cm⁻¹, while Schiff base-modified polymer beads exhibit $v_{C=O}$ stretching frequency of 1643 to 1652 cm⁻¹ along with characteristics $v_{C=N}$ stretching frequency of 1601 to 1602 cm⁻¹, suggesting the formation of Schiff base-modified polymer chain. Shifting of the $v_{C=N}$ stretching frequency to lower wavenumber in the polymer-anchored vanadium complexes signifies coordination of azomethine nitrogen to vanadium [49].

In all the ligands except I, –NH and –OH functional groups appear jointly as a broad band from 3395–3358 cm⁻¹, whereas corresponding vanadium complexes (**2** and **3**) show one medium sharp band at 3243–3242 cm⁻¹ due to V_{N-H} . All the polymer-bound metal complexes, PS-[V^{IV}O(Ae-Eol)] (**1**), PS-[V^{IV}O(Hy-Eda)] (**2**), and PS-[V^{IV}O(HyP-Eda)] (**3**), show one strong and sharp peak at 929–964 cm⁻¹ assigned to $V_{V=O}$ stretch [49]. Recycled catalysts show a similar IR spectral pattern except slightly reduced intensity (shown in Figures S7–S9), indicating no change in their molecular skeleton.

S.No.	Compounds	V _{C=0}	V _{C=N}	V _{O-H}	V _{N-H}	V _{V=0}
1	PS-CHO	1700	_	_	_	_
2	PS-[Ae-Eol] (I)	1643	1601	3395	-	_
3	PS-[Hy-Eda] (II)	1649	1602	3358	Merged with –OH	_
4	PS-[HyP-Eda] (III)	1652	1602	3373	Merged with –OH	_
5	PS-[V ^{IV} O(Ae-Eol)] (1)	1632	1604	3298	-	964
6	PS-[V ^{IV} O(Hy-Eda)] (2)	1636	1586	-	3243	940
7	PS-[V ^{IV} O(HyP-Eda)] (3)	1630	1603	-	3342	929

Table 1. Selected FT-IR data of polymer-anchored ligands and metal complexes.



Figure 1. UV-vis spectra of PS-[V^{IV}O(Ae-Eol)] (1), PS-[V^{IV}O(Hy-Eda)] (2), and PS-[V^{IV}O(HyP-Eda)] (3) recorded by dispersed in Nujol.

Electronic spectral data of the polymer-grafted **1**, **2**, and **3** were recorded by dispersing in Nujol. Metal complex-anchored polymer beads show medium to low intensity absorbance due to the poor loading of the metal complexes into the polymeric matrix. Electronic spectra of **1**, **2**, and **3** are displayed in Figure 1 and selected absorbance bands are listed in Table S1. All three polymer-anchored vanadium complexes show very low intensity but detectable electronic transitions. Bands from 969 to 756 nm are assigned to *d*-*d* transitions. Ligand to metal charge transfer bands may be observed from 691 to 528 nm. All three polymer-anchored vanadium complexes show *n*- π * transitions from 362 to 337 nm. Bands at 326 to 290 nm may be attributed to π - π * transitions. However, it is very difficult to predict the exact nature of the electronic transitions, but the electronic spectra definitely confirm the presence of metal complexes in the polymeric chain.

3.2. SEM and EDX analysis

Morphological changes during the preparation of polymer-grafted metal complexes were recorded by field emission scanning electron micrograph (FE-SEM). Selected FE-SEM images of pure and metal-anchored polymer beads are shown in Figure 2 and their corresponding



Figure 2. FE-SEM images of (A) Merrifield's peptide resin (PS), (B) oxidized chloromethylated polystyrene (PS-CHO), (C) PS-[Hy-Eda] (II), and (D) PS-[V^{IV}O(Hy-Eda)] (2).



Figure 3. EDX profile of (A) pure chloromethylated polystyrene (PS), (B) oxidized chloromethylated polystyrene (PS-CHO), (C) PS-[Hy-Eda] (II), and (D) PS-[V^{IV}O(Hy-Eda)] (**2**).

		Metal loading (mmol g ⁻¹)				
S.No.	Complexes	(EDX)	TGA	(AAS)	(AAS)*	
1	PS-[V ^V O(Ae-Eol)] (1)	4.19	1.6	0.41	0.38	
2	PS-[V ^v O(Hy-Eda)] (2)	3.02	5.2	0.61	0.55	
3	PS-[V ^V O(HyP-Eda)] (3)	2.18	1.9	0.21	0.19	

*Values for recycled catalysts.

EDX plots are shown in Figure 3. Grafting of the vanadium complex resulted in roughening of the upper surface of polymer beads. Energy dispersive X-ray analysis plot of pure polymer bead (Figure 3(A)) shows carbon and chlorine signals, whereas an additional oxygen signal is observed in the oxidized polymer bead (Figure 3(B)) along with carbon and chlorine signals, indicating partial oxidation of polymer bead. Ligand-anchored polymer bead (Figure 3(C)) shows nitrogen content along with carbon and oxygen while metal complex-anchored polymer bead (Figure 3(D)) exhibits the signals of C, N, and O along with the signal of V.

Semi-quantitative measurement of polymer-anchored metal complexes by EDX indicates 4.19, 3.02, and 2.18 mmol g⁻¹ vanadium content in **1**, **2**, and **3**, respectively. Actual metal loading into the polymeric matrix was confirmed by AAS technique (listed in Table 2 along with the metal loading calculated from TGA and EDX analysis). All these plots and signals suggest successful grafting of the vanadium complexes into the polymeric chain.

3.3. Thermogravimetric analysis

Thermal stability of polymer-anchored vanadium complexes was examined by TGA analysis at a heating rate of 20 °C/minute in air from 40 to 750 °C. TGA plots along with DTA plots of polymer-anchored metal complexes PS-[V^{IV}O(Ae-Eol)] (1), PS-[V^{IV}O(Hy-Eda)] (2), and PS-[V^{IV}O(HyP-Eda)] (3) are presented in Figure 4(A)–(C). Complex 1 is stable upto 418 °C, whereas 2 and 3 show thermal stability upto 442 °C. TGA profile of 1, 2, and 3 proceeds with an endothermic decomposition of 1.7, 1.4, and 3%, respectively, from 46 to 55 °C, due to



Figure 4. TGA/DTA plots of polymer-anchored complexes (A) PS-[V^{IV}O(Ae-Eol)] (1), (B) PS-[V^{IV}O(Hy-Eda)] (2), and (C) PS-[V^{IV}O(HyP-Eda)] (3).

desorption of entrapped moisture and gasses from the polymer cage. Complex **1** produces two endothermic peaks, one at 387 °C because of the melting of the polymer, followed by an endothermic peak from 418 to 550 °C associated with the breakdown of polymer

backbone as well as the ligand structure. This is supported by the fact that the TGA plot of **1** shows a massive weight loss at that temperature range (Figure 4(A)). DTA plot of **2** shows one broad endothermic peak at 372 °C for slow melting of the polymer bead. Finally, decomposition of the polymeric structure followed by decomposition of ligand structure is observed for **2** from 442 to 549 °C. Existence of two endothermic peaks in that temperature range is consistent with this interpretation (Figure 4(B)).

Complex **3** also shows one endothermic peak at 418 °C because of the melting of the polymer bead. An exothermic peak at 444 °C and an endothermic peak at 487 °C originate from the decomposition of polymer chain as well as the ligand, supported by the huge weight loss (Figure 4(C)). An approximate vanadium loading was also calculated from residual amount of vanadium oxide (V_2O_5); **1**, **2**, and **3** contain 1.6, 5.2, and 1.9 mmol/g of vanadium, respectively (listed in Table 2).

3.4. EPR studies

To confirm the oxidation state of vanadium, room temperature X-band EPR spectra of $PS-[V^{IV}O(Ae-EoI)]$ (1), $PS-[V^{IV}O(Hy-Eda)]$ (2), and $PS-[V^{IV}O(HyP-Eda)]$ (3) are recorded and



Figure 5. X-band EPR spectra of (A) PS-[V^{IV}O(Ae-Eol)] (1), (B) PS-[V^{IV}O(Hy-Eda)] (2), and (C) PS-[V^{IV}O(HyP-Eda)] (3) at room temperature.

shown in Figure 5. Complexes 1, 2, and 3 show an axially symmetrical signal characteristic of V⁴⁺ [49, 50]. Hyperfine lines appearing in Figures 5(A)–(C) are due to the coupling of a single unpaired electron of V⁴⁺ to its own nucleus of spin value 7/2 (2nl + 1 = 8). All three compounds show well-resolved hyperfine spectra in both parallel and perpendicular regions. Out of expected 16 lines (8 in perpendicular orientation and 8 in parallel orientation), all of the perpendicular transitions and 4 transitions in parallel orientation are observed. The resolved hyperfine EPR spectra imply that the vanadium centers are well dispersed in the polymeric matrix and practically no vanadium–vanadium interactions exist.

3.5. Catalytic activities studies

3.5.1. Oxidation of alkenes

Catalyst precursors PS-[V^{IV}O(Ae-Eol)] (1), PS-[V^{IV}O(Hy-Eda)] (2), and PS-[V^{IV}O(HyP-Eda)] (3) were used for oxidation of a number of alkenes, namely styrene, cyclohexene, allylbenzene, and *cis*-cyclooctene in the presence of aqueous hydrogen peroxide. Oxidation of styrene was considered as a model reaction with 1 as the representative catalyst. Previously, styrene oxide (bep), benzaldehyde (bzh), benzoic acid (bza), phenylacetaldehyde (bzy), and 1-phenylethane-1,2-diol (ped) were reported during the catalytic oxidation of styrene by H_2O_2 (shown in Scheme 2) [4, 51, 52].

In the present study, two new oxidation products, 2-hydroxy-1-phenylethanone (hep) and 2-phenylacetaldehyde (pac), were identified along with the five expected products. For maximizing the oxidation of styrene, a number of parameters such as amount of catalyst, amount of oxidant, amount of solvent, and nature of the solvent were studied.

Figure 6(A) displays the effect of amount of catalyst on the oxidation of styrene. Three different amounts of 1, 0.015, 0.020, and 0.025 g, were considered while reacting fixed amounts of styrene (0.52 g, 5 mmol) with H_2O_2 (1.7025 g, 15 mmol) in 10 mL of methanol at 70 °C; 87.3% product conversion was observed in six hours by 0.015 g catalyst. Increasing



Scheme 2. Main oxidation products of styrene catalyzed by 1, 2, and 3 in the presence of hydrogen peroxide.

S.No.	Cat.	Substrates	Amount (mg)	Sub:Ox	Solvent amount (mL)	Solvent	% Conver- sion	TOF (h ⁻¹)
1	1	Styrene	15	1.3	10	Methanol	87 3	116.02
2	1	Styrene	20	1:3	10	Methanol	90.9	90.61
3	1	Styrene	25	1:3	10	Methanol	93.5	74.54
4	1	Styrene	15	1:2	10	Methanol	86.7	115.23
5	1	Styrene	15	1:4	10	Methanol	95.1	126.34
6	1	Styrene	15	1:4	5	Methanol	99.9	132.72
7	1	Styrene	15	1:4	15	Methanol	91.3	121.37
8	1	Styrene	15	1:4	5	Acetonitrile	99.5	132.28
9	1	Styrene	15	1:4	5	Ethanol	97.8	129.94
10	1	Styrene	15	1:4	5	THF	99.1	131.72
11	1	Styrene	15	1:4	5	DMF	15.4	20.40
12	1	Styrene	15	1:4	5	Acetone	92.0	131.72
13	1	Cyclohexene	15	1:4	5	Methanol	95.1	126.42
14	1	Allylbenzene	15	1:4	5	Methanol	77.5	102.93
15	1	Cis-cyclooc- tene	15	1:4	5	Methanol	83.0	110.34
16	2	Styrene	15	1:4	5	Methanol	88.1	79.75
17	2	Cis-cyclooc- tene	15	1:4	5	Methanol	32.5	29.44
18	2	Cyclohexene	15	1:4	5	Methanol	79.1	71.66
19	2	Allylbenzene	15	1:4	5	Methanol	58.7	53.16
20	3	Cyclohexene	15	1:4	5	Methanol	92.8	236.74
21	3	Cis-cyclooc- tene	15	1:4	5	Methanol	99.2	253.05
22	3	Styrene	15	1:4	5	Methanol	95.4	243.31
23	3	Allylbenzene	15	1:4	5	Methanol	81.2	207.03

Table 3. Conversion % and TOF values of catalytic oxidation of styrene, cyclohexene, allylbenzene, and *cis*-cyclooctene using 1, 2, and 3 in 6 h under various reaction conditions.

the catalyst amount from 0.015 to 0.020 g, percent conversion increases merely 3.6%. Further increase in the catalyst amount from 0.020 to 0.025 g, percent conversion also increases from 90.9 to 93.5%, which is quite marginal. Hence, 0.015 g catalyst was considered optimal.

To optimize the amount of oxidant (30% H_2O_2), three different styrene to H_2O_2 ratios, i.e. 1:2, 1:3, and 1:4, were used for fixed amounts of styrene (0.52 g, 5 mmol) and catalyst precursor (0.015 g) in 10-mL methanol at 70 °C temperature for 6 h. 1:4 styrene to H_2O_2 ratio produced 95.1% product conversion. It is clear from Figure 6(B) that 1:2 and 1:3 show only 86.7 and 87.3% conversion, respectively, so 1:4 ratio of styrene to H_2O_2 was set as optimal.

The impact of volume of solvent was checked by taking 5, 10, and 15 mL of methanol while using fixed amounts of styrene (0.52 g, 5 mmol), 30% H_2O_2 (2.27 g, 20 mmol), and catalyst precursor (0.015 g) at 70 °C temperature for 6 h (shown in Figure 6(C)).

In 5 mL of methanol, 0.015 g of catalyst exhibit maximum 99.9% conversion. Increasing the solvent amount from 5 to 10 mL, percent conversion decreases from 99.9 to 95.01%. Conversion continues to decline with increasing solvent from 10 to 15 mL, which may be due to the less effective collision among the reactant molecules in more diluted solution. Thus, 5 mL of methanol is considered the best.

Effect of solvent polarity on the catalytic oxidation of styrene was also examined. Six different solvents, methanol (MeOH), ethanol (EtOH), acetonitrile (ACN), tetrahydrofuran (THF), acetone, and dimethyl formamide (DMF), were considered while keeping the other reaction parameters fixed, i.e. styrene (0.52 g, 5 mmol), 30% H₂O₂ (2.27 g, 20 mmol), catalyst precursor



Figure 6. (A) Effect of amount of 1 on the oxidation of styrene. (B) Effect of amount of H_2O_2 on the oxidation of styrene. (C) Effect of amount of solvent (methanol) on the oxidation of styrene. (D) Effect of nature of solvent on the oxidation of styrene. For reaction conditions see text.

(0.015 g), 5 mL solvent, 70 °C temperature, and 6 h reaction time. Figure 6(D) shows that of the six solvents, quantitative (more than 99%) oxidation of styrene was observed in MeOH, EtOH, ACN, and THF while in acetone catalytic oxidation proceeds up to 92%; DMF is not a suitable solvent for the catalytic oxidation of styrene with only 15.4% of product observed. Hence, easily available and cheaper methanol was used to perform all other catalytic oxidation reactions. Various reaction conditions for the catalytic oxidation of styrene are summarized in Table 3 in which serial number 6 represents the optimized conditions, which is 5 mmol (0.52 g) styrene, 20 mmol (2.27 g) 30% H₂O₂, 0.015 g catalyst precursor, 5 mL methanol, 70 °C temperature, and 6-h reaction time.

Catalytic oxidation of styrene under optimized reaction conditions by **1** exhibits 99.9% conversion with TOF value $132.72 h^{-1}$ and by **3** shows 95.4% conversion with TOF value 243.31 h⁻¹, while using **2** only 88.1% conversion is achieved with TOF value 79.75 h⁻¹ (shown in Figure 7). Conversion % along with the % selectivity of various oxidation products of styrene catalyzed by **1**, **2**, and **3** under optimized reaction conditions is shown in Table S2. **1** exhibits acetophenone as a major product with selectivity of 34.10%, whereas **2** and **3** produced benzaldehyde as a major product with selectivity 31.9 and 39.13%, respectively. A blank reaction under the same optimized reaction conditions shows only 15% product conversion. Although catalytic oxidation of styrene can be found in a number of reports [4,

53–60], comparing with the existing literature data (shown in Table S3), **1**, **2**, and **3** can be a better choice over the reported catalysts, in terms of overall % conversion, reaction time, and relatively moderate reaction conditions.

Liquid phase catalytic oxidation of cyclohexene was tested by **1**, **2**, and **3** under similar optimized reaction conditions as described in the oxidation of styrene, i.e. 5 mmol cyclohexene, 0.015 g catalyst precursor, and 20 mmol (2.27 g) 30% H₂O₂ reacted in 5-mL methanol at 70 °C temperature for 6 h. Catalytic oxidation of cyclohexene by **1**, **2**, and **3** in the presence of hydrogen peroxide produces 2-cyclohexene-1-ol (che), cyclohexeneepoxide (och) and cyclohexane 1,2-di-ol (chd) as reported in the literature [61–64] along with a fourth product, i.e. 2-hydroxycyclohexanone (hch) (shown in Scheme 3). Oxidation products were confirmed by GC-MS and quantified by GC.

Figure 8 compares the catalytic efficiency of **1**, **2**, and **3** for the oxidation of cyclohexene. Conversion % along with the % selectivity of the individual oxidation products is listed in Table S4. Figure 8 shows that **1** and **3** are more efficient toward catalytic oxidation of cyclohexene than **2**.

Catalyst **1** exhibits 95.1% conversion with 126.42 h⁻¹ TOF and **3** shows 92.8% conversion with 236.74 h⁻¹ TOF. Least catalytic activity was observed by **2** which shows only 79.1% conversion with TOF of 71.66 h⁻¹. In terms of % selectivity, again catalysts **1** and **3** produce 2-cyclohexene-1-ol as a major product with 43.29 and 43.40% selectivity, respectively, while catalyst **2** produces cyclohexane 1,2-diol as a major oxidation product with 47.19% selectivity. Under similar optimized reaction conditions, a blank reaction shows only 4.7% conversion. Although **2** functions little less effectively in comparison to **1** and **3**, with respect to the available literature [4, 53, 61, 65–67] (shown in Table S5), **1**, **2**, and **3** emerge as better candidates for the catalytic oxidation of cyclohexene.

Catalytic oxidation of allylbenzene by **1**, **2**, and **3** in the presence of $30\% H_2O_2$ is evaluated. Oxidation of allylbenzene produces benzaldehyde (bzh), benzoic acid (bza), 1-phenylprop-2-en-1-one (peo), 2-phenylacetaldehyde (pac), and 3-phenylacrylaldehyde (cal) as oxidation



Scheme 3. Main products obtained by catalytic oxidation of cyclohexene using 1, 2, and 3.



Scheme 4. Oxidation products of allylbenzene catalyzed by 1, 2, and 3 in the presence of hydrogen peroxide.



Figure 7. Impact of 1, 2, and 3 on catalytic oxidation of styrene. Reaction conditions: styrene (0.52 g, 5 mmol), catalyst precursor (0.015 g), 30% H_2O_2 (2.27 g, 20 mmol), 70 °C temperature, and 6-h reaction time.



Figure 8. Influence of 1, 2, and 3 on catalytic oxidation of cyclohexene. Reaction conditions: cyclohexene (5 mmol), catalyst precursor (0.015 g), 30% H_2O_2 (2.27 g, 20 mmol), 70 °C temperature, and 6h reaction time.

products (shown in Scheme 4). Identity of the products was confirmed by GC-MS analyses.

The impact of **1**, **2**, and **3** on the catalytic oxidation of allylbenzene as a function of time has been studied and presented in Figure 9. Figure 9 shows that **1** and **3** are more influential than **2** toward catalytic oxidation of allylbenzene, but this time **3** functions slightly better than **1**. Catalyst **3** shows 81.2% conversion with TOF value of 207.03 h⁻¹ and catalyst **1** shows 77.5% conversion with TOF 102.93 h⁻¹. Catalyst **2** leads to only 58.7% conversion accompanied by TOF value of 53.16 h⁻¹. Detailed % conversion and product selectivity of the different oxidation products of allylbenzene are documented in Table S4.



Figure 9. Effect of 1, 2, and 3 on catalytic oxidation of allylbenzene. Reaction conditions: allylbenzene (5 mmol), catalyst precursor (0.015 g), 30% H₂O₂ (2.27 g, 20 mmol), 70 °C temperature, and 6-h reaction time.

With 40.47, 32.77, and 32.50% of selectivity, benzaldehyde appears as a major product during the catalytic oxidation of allylbenzene by catalysts 3, 1, and 2, respectively. From Table S4, it is clear that all three catalysts show similar trends in the product distribution during the oxidation of allylbenzene: benzaldehyde > benzoic acid > 1-phenylprop-2-en-1one > 2-phenylacetaldehyde > 3-phenylacrylaldehyde. A blank reaction under the same optimized reaction conditions exhibits only 2.5% product conversion. Catalytic oxidation of allylbenzene reported in the literature is limited [68-72]. However, with respect to the available literature (shown in Table S7), 1, 2, and 3 appear as potential candidates for the catalytic oxidation of allylbenzene under moderate reaction conditions.

Under the optimized reaction conditions, 1, 2, and 3 were employed for the catalytic oxidation of cis-cyclooctene (Figure 10). Homogeneous or heterogeneous catalytic oxidation of cis-cyclooctene produces cyclooctene oxide (ocn) as a major product. Apart from this, a number of oxidation products, cyclooctane-1,2-diol, 2-cycloocten-1-one, 2-cycloocten-1-ol, cyclooctanol, and cyclooctanone, were reported [73-80]. In the current study, cyclooctene oxide (ocn) is a major product along with small percents of cyclooctane-1,2-diol (cod) and 2-cycloocten-1-one (coe) (shown in Scheme 5).

Identity of the oxidation products is confirmed by GC-MS analyses. GC-MS chromatograph exhibits split cyclooctene oxide peak. Fragmentation pattern of each of the split peaks matches with the standard fragmentation pattern of cyclooctene oxide (by library search) at 70 eV. Hence, formation of two isomeric structures, cis- and trans- isomer of cyclooctene oxide, during the catalytic oxidation of cis-cyclooctene is proposed. Under the optimized reaction conditions, % conversion and % selectivity of the isolated products of catalytic oxidation of *cis*-cyclooctene with H_2O_2 in the presence of **1**, **2**, and **3** are listed in Table S5. Catalyst **3** shows a maximum of 99.2% conversion with TOF of 253.05 h^{-1} , and catalyst **1** produces 83.0% product conversion with TOF of 110.34 h⁻¹; only 32.5% product conversion is observed by 2 with TOF value of 29.44 h⁻¹. These values are quite high in comparison to the data reported by Glaser et al. [74], Nomiya et al. [75], Cai et al. [78], and Carreon et al. [80],

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Figure 10. Impact of **1**, **2**, and **3** on catalytic oxidation of *cis*-cyclooctene. Reaction conditions: *cis*-cyclooctene (5 mmol), catalyst precursor (0.015 g), 30% H_2O_2 (2.27 g, 20 mmol), 70 °C temperature, and 6-h reaction time.



Scheme 5. Various oxidation products of *cis*-cyclooctene catalyzed by 1, 2, and 3 in the presence of hydrogen peroxide.

whereas Nakagaki *et al.* [79] and Saberyan *et al.* [77] reported few catalysts of close catalytic properties to those of **1**, **2**, and **3** (Table S9). Only 1% product conversion is observed during the blank reaction.

A comparative % conversion vs. reaction time plot of catalytic oxidation of alkenes (styrene, cyclohexene, allylbenzene, and *cis*-cyclooctene) by **1**, **2**, and **3** is shown in Figure 11(A)–11(C). Although the three catalysts function for oxidation of styrene, cyclohexene, allylbenzene, and *cis*-cyclooctene, overall functionality of **1** and **3** is much better than **2**. Under the optimized reaction conditions, in the presence of **3**, catalytic oxidations of styrene, cyclohexene, allylbenzene, and *cis*-cyclooctene show 95.4, 92.8, 81.2, and 99.24% conversion, respectively. Catalyst **1** produces 99.9, 95.1, 77.5, and 83.0% conversion for the oxidation of styrene, cyclohexene, allylbenzene, and *cis*-cyclooctene, respectively, under the same optimized reaction conditions, whereas only 88.1, 79.1, 58.7, and 32.5% conversion was achieved by **2**.

Table 3 indicates that among styrene, cyclohexene, allylbenzene, and *cis*-cyclooctene, **1** is more effective toward the oxidation of styrene and cyclohexene, while **3** is more effective toward oxidation of allylbenzene and *cis*-cyclooctene. In conclusion, **3** is more versatile than **1** and **2** in terms of oxidation of various alkenes.



Figure 11. Conversion % against reaction time for the catalytic oxidation of styrene, cyclohexene, allylbenzene, and *cis*-cyclooctene by (A) $PS-[V^{IV}O(Ae-Eol)]$ (1), (B) $PS-[V^{IV}O(Hy-Eda)]$ (2), and (C) $PS-[V^{IV}O(Hy-Eda)]$ (3) under optimized reaction conditions.

		Catalysts				
	—	1	2	3		
S.No.	Substrates	% Conversion				
1	Styrene	99.9	88.1	95.4		
2	Styrene*	92.5	84.0	91.6		
3	Styrene**	90.3	83.6	90.2		
4	Cyclohexene	95.1	79.1	92.8		
5	Cyclohexene*	90.7	75.0	86.9		
6	Cyclohexene**	89.4	74.6	86.2		
7	Allylbenzene	77.5	58.7	81.2		
8	Allylbenzene*	74.1	56.3	75.6		
9	Allylbenzene**	73.5	55.4	75.1		
10	<i>Cis</i> -cyclooctene	83.0	32.5	99.2		
11	Cis-cyclooctene*	82.7	27.3	94.1		
12	Cis-cyclooctene**	80.3	26.9	93.5		

Table 4. Conversion % of catalytic oxidation of styrene, cyclohexene, allylbenzene, and *cis*-cyclooctene using fresh and recycled 1, 2, and 3 under optimized reaction conditions.

*Values for first recycled catalysts.

**Values for second recycled catalysts.

3.5.2. Study of leaching of vanadium from the polymer-bound catalysts and test of recyclability

Reusabilities of the polymer-anchored vanadium catalysts were checked. After the catalytic reactions, **1**, **2**, and **3** were washed with methanol and dried in an oven at 120 °C up to 24 h. Under the same optimized reaction conditions, used catalysts show % conversion close to that of the fresh one up to 3 cycles. Detailed % conversion of fresh and recycled catalysts is listed in Table 4. Slightly reduced activities in the first cycle may be explained by the fact that a few physically adsorbed vanadium complexes were lost from the polymeric matrix during the catalytic reactions. AAS analyses of the used catalysts (mentioned in Table 2) show a little less but close vanadium loading in comparison to that of fresh catalysts, suggesting partial leaching of vanadium center from the polymeric matrix. Hence, **1**, **2**, and **3** can be considered as recyclable and effective catalysts for the oxidation of alkenes.

FT-IR spectra of recycled catalysts **1**, **2**, and **3** are shown in Figures S7–S9. Comparable FT-IR spectral patterns of the used catalysts to that of the fresh catalysts confirm the presence of catalytic center in the used catalysts and support their recyclability.

4. Conclusion

Three chloromethylated polystyrenes cross-linked with divinylbenzene-functionalized Schiff bases PS-[Ae-EoI] (I), PS-[Hy-Eda] (II), and PS-[HyP-Eda] (III) were synthesized by reacting oxidized chloromethylated polystyrene with 2-(2-aminoethoxy)ethanol (Ae-EoI), N-(2-hydroxyethyl)ethylenediamine (HyP-Eda), and N-(2-hydroxpropyl)ethylenediamine (HyP-Eda), respectively. Corresponding monomeric vanadium(IV) complexes of the Schiff base ligands were isolated by reacting [VO(acac)₂] with I, II, and III. FT-IR, UV-vis spectral studies, and EDX analyses confirm the successful anchoring of the vanadium complexes on the polymeric chain. Vanadium loadings into the polymeric chain were calculated by AAS analysis. Catalysts 1, 2, and 3 showed thermal stability up to 430, 340, and 433 °C, respectively, as scrutinized by TGA analyses. EPR analyses established magnetically dilute or well-dispersed attachments of 1, 2, and 3 on the polymeric support. PS-[V^{IV}O(Ae-EoI)] (1), PS-[V^{IV}O(Hy-Eda)] (2), and

PS-[V^{IV}O(HyP-Eda)] (**3**) efficiently catalyzed oxidation of a range of alkenes. Overall performance of **2** is less than **1** and **3** toward the catalytic oxidation of alkenes. Between **1** and **3**, catalyst **1** showed better catalytic activity toward the oxidation of styrene and cyclohexene (99.86% and 95.12% by **1** while **3** shows 95.42 and 92.84%, respectively). However, **3** showed more effectiveness toward the catalytic oxidation of *cis*-cyclooctane and allylbenzene than **2**. Under optimized reaction conditions, 99.24% conversion for *cis*-cyclooctene and 81.19% conversion for allylbenzene were observed by **3** while **2** showed only 83.02 and 77.45% conversion. Uncomplicated and straightforward synthesis of polymer-anchored monomeric vanadium(IV) Schiff base complexes studied here along with their thermal stability, recyclability without much loss of catalytic activity, and effective catalytic efficiency toward a wide range of alkenes in the presence of an ecofriendly oxidizing agent, hydrogen peroxide, makes them cost-effective and ecofriendly catalysts for the catalytic oxidation of alkenes.

Supplementary material

FT-IR, UV-vis data, and figures for the polymer-anchored ligands and metal complexes along with % conversion, TOF, and % selectivity of individual oxidation products of various alkenes catalyzed by 1, 2, and 3 under optimized reaction conditions are submitted as Supporting Materials.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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