Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Research paper

Development of a polymer embedded reusable heterogeneous oxovanadium (IV) catalyst for selective oxidation of aromatic alkanes and alkenes using green oxidant

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ARTICLE INFO

Keywords: Oxidation Aromatic alkanes Oxovanadium(IV) catalyst Aromatic alkenes 30% aqueous H₂O₂

ABSTRACT

A new heterogeneous polymer supported solid phase oxovanadium(IV) catalyst was synthesized successfully. The designed catalyst furnished excellent results in the oxidation reactions of various aromatic alkanes, e.g. toluene, para-xylene, mesitylene. The polymer supported vanadium complex was proved also an efficient catalyst for the oxidation of aromatic alkenes, like substituted styrenes, trans-stilbene, etc. under mild reaction conditions. The supported catalyst was nicely elucidated by SEM-EDAX, TGA, FT-IR and UV-Vis spectral analysis. The catalytic activity was tested in the presence of an environment-friendly oxidant, 30% aqueous H_2O_2 during the oxidation of broad range of substrates. Another important fact is that the designed oxovanadium(IV) catalyst is heterogeneous in nature. Moreover, the newly synthesized oxovanadium(IV) complex exhibited a notable recoverability and it could be recycled up to six runs devoid of any prominent reduction in catalytic behavior.

1. Introduction

The catalytic oxidation process contributes a major and fundamental area in the industry as well as in academic world. Catalytic oxidation reaction of aromatic alkenes and sp³ C-H bonds of the aromatic alkanes to the corresponding oxygenated products is an interesting and challenging part of investigation in the catalytic field [1]. The products isolated from the catalytic oxidation reactions of aromatic alkanes (hydrocarbons) are the essential intermediates for many agrochemicals, chemical feedstocks, and polymers. Such products are utilized as preliminary materials for fragrances and pharmaceuticals. Usually alkyl (-CH₃, -CH₂CH₃) substituted aromatic hydrocarbon holds inactive sp³ C–H bonds. These hydrocarbons undergo oxidation process to deliver some value added oxidized products [2]. The most promising product is benzaldehyde, due to its amazing consumption in manufacturing of preservatives, dyes, perfumes, plasticizers and pharmaceuticals [3]. Aromatic alkenes like styrene, trans-stilbene when subjected to catalytic oxidation process consequence to their corresponding carbonyl compounds or carboxylic acids. Those carbonyl or

carboxylic acid compounds have enormous importance in a large number of organic transformations [4]. Several metal based oxides like Ru(VIII)/Os(VIII) oxides are reported for this transformation [5]. But this method encompasses several drawbacks from the viewpoints of safety and chemical wastes. Hence an alternative and advanced approach is necessary for the catalytic system to the development of sustainable industrial organic conversions. Environmentally secure and greener processes are also desirable for economically feasible catalytic systems [6]. The previously achieved oxidation reactions were reported in presence of homogeneous metal catalysts, experiencing a major drawback. After completion of the reaction the homogeneous catalyst cannot be isolated from the reaction system. Further activity of the costly catalysts in subsequent cycle is not possible accordingly. In this state, one cannot ignore the possibility of resulting product contamination with the catalyst, which limits their extensive purpose in the industrial process. Thus the oxidation reactions of aromatic alkanes/ alkenes are favored in presence of polymer-supported heterogeneous catalysts with reasonable thermal stability in contrast to their homogeneous analogues. In recent times, various solid supports, like zeolite

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https://doi.org/10.1016/j.ica.2019.04.037

Received 9 September 2018; Received in revised form 18 April 2019; Accepted 18 April 2019 Available online 20 April 2019

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[7], alumina [8], amorphous silicates [9], polymers [10] and MCM-41 [11] are reported for the establishment of different heterogeneous metal complexes. Amino-polystyrene is an effective heterogeneous solid, is privileged to its good stability and reusuability [12]. Vanadium (IV) ion is most effective one for the oxidation of hydrocarbons [13,14] with most of the recognized oxidants: H₂O₂, tert-butyl hydroperoxide, molecular oxygen [15–20] under heterogeneous phase. The important fact for using vanadium instead of other metals is that it is a low cost metal. Secondly it also carries more than one oxidation states suitable for various organic electron-transfer reactions [21,22]. Vanadium complexes having +4 or +5 oxidation states are established compounds for successful employing in synthetic, biological and material chemistry section [23,24]. Until now, many d-block transition metal compounds of manganese [25], iron [26], nickel [27], copper [28] and cobalt [7b] with polymer supported ligands are reported throughout the heterogeneous catalytic liquid phase selective partial oxidation reactions of aromatic hydrocarbon C-H oxidation using different oxidants. Polymer supported transition metal catalyst are proved very efficient for the partial and selective oxidation of aromatic hydrocarbons to the corresponding aldehydes under mild reaction conditions [25–28]. Among these metals, vanadium is preferred over manganese, iron and copper on account of the corrosive nature of these metal ions. From environmental concern vanadium is relatively non-toxic and 20th most abundant element in the universe [29]. Several works on aromatic alkane/alkene oxidations are typically available by homogeneous vanadium catalysts [30]. But a severe issue was found with these homogeneous catalysts since they could not be straightforwardly removed or recycled. The aromatic alkane/alkene oxidations were performed with heterogeneous vanadium catalyst by the oxidant, tert-butyl hydroperoxide accordingly [17,20]. But tert-butyl hydroperoxide is not an ecofriendly oxidizing agent, thus hydrogen peroxide can be used as a mild substitute for the present oxidation. From the perspective of green amendment, hydrogen peroxide is not only an interesting 'green' and cheaper oxidant, it is more reactive than molecular O_2 [15]. Pertaining to the liquid phase oxidation using H₂O₂, the VO(acac)₂ catalyst was very well known to furnish oxidized product benzaldehyde by partial oxidation of toluene [31]. Rezaei et al. have also investigated the same oxidized product from toluene by environmentally safe and economic oxidant H₂O₂ in presence of vanadium phosphate catalyst [3]. The attractive point of our system is the liquid phase partial oxidation of substituted toluenes over polymer grafted PS-VO-naph catalyst to produce benzaldehydes with reasonable selectivity. Parallel report on the liquid phase oxidation of styrene by H2O2 was also evaluated using Co-Ag co-doped ZnO catalyst [32]. The Cr-ZSM-5 zeolite catalyzed selective oxidation of styrene to benzaldehyde was reported using H₂O₂ as an efficient oxidant [33]. Benzaldehyde was formed with significant selectivity by the liquid phase partial oxidation of styrene; as the styrene oxide produced in the first step converted into benzaldehyde through a nucleophilic attack of H_2O_2 on styrene oxide [33,34]. In the present experiment the PS-VO-naph complex was successfully recognized as heterogeneous and recyclable catalyst for the liquid phase oxidation of styrene to benzaldehyde with satisfactory yield. The oxidation process experienced with H₂O₂ liberates water as the only sustainable by-product [27]. Acetonitrile has been utilized instead of the solvents containing sulphur (e.g. DMSO) producing corrosions, serious environmental hazards, and health issues [35]. Here, we have prepared an efficacious heterogeneous catalyst, viz. a polystyrene grafted vanadium Schiff base complex, [PS-VO-naph], to oxidize a range of substituted aromatic hydrocarbons with 30% aqueous H₂O₂. The general procedure, characterization and the overall experimental phenomena have been illustrated briefly.

2. Experimental

2.1. Materials

Poly(styrene-*co*-divinyl benzene) 2% cross linked, (Art. No. 434442-50G) was purchased from Aldrich, USA. 30% aqueous hydrogen peroxide was supplied by SRL. Other organic reagents were received from Fluka or Merck. By following the standard procedures, necessary solvents were perfectly dried and distilled before use. All other chemicals were used for the reactions as taken without additional treatment for refinement.

2.2. Characterization methods in solid state

FT-IR (Fourier transform infrared) spectra of the materials were recorded using KBr disc in Perkin-Elmer FT-IR 783 spectrophotometer. The UV-Vis spectra of the synthesized ligand and oxovanadium(IV) catalyst were recorded in solid state with the help of a Shimadzu doubled beam spectrophotometer (UV-2401 PC) attached with an integrating sphere in the diffuse reflectance mode by taking BaSO₄ disk as internal reference. The thermal analyzer Mettler-Toledo TGA-DTA 851e under N2 flow was operated for the thermogravimetric (TGA) analysis of the materials. Scanning electron microscope (SEM) (ZEISS EVO40, England) having EDAX facility was used to compare the morphological alteration of the supported ligand and catalyst. Transmission electron microscopy (TEM) images were recorded with a JEOL JEM 2010 transmission electron microscope operating at 200 kV, and the necessary samples were prepared by mounting an ethanol-dispersed sample on a lacey carbon Formvar coated Cu grid. Powder X-ray diffraction (PXRD) pattern of the materials was obtained by using a Bruker D8 Advance X-rav diffractometer using Ni-filtered Cu Kα $(\lambda = 0.15406 \text{ nm})$ radiation. Elemental analysis of the materials was attempted with a Perkin Elmer 2400C elemental analyzer. The Varian AA240 atomic absorption spectrometer was set to measure the vanadium metal content in oxovanadium catalyst. The oxidized products were recognized over a Varian 3400 gas chromatograph (GC) fitted to a 30 m CP-SIL 8CB capillary column with a facility of flame ionization detector.

2.3. Synthesis of amino polystyrene anchored azo ligand, PS-naph

The para-amino polystyrene (1) was prepared from 2% crosslinked poly(styrene-*co*-divinyl-benzene) according to the available literature sources [36]. Then the ligand was prepared by following the literature procedure [37]. 1 g of para-amino polystyrene (1) was suspended in 20 mL methanol to which a 20 mL methanolic solution of 0.5 g of 1-nitroso-2-naphthol was added upon constant stirring and it was refluxed for 24 h. The green colored PS-naph ligand (2) was obtained after the end of the reaction. The resultant mixture was set to filter and washing was performed with methanol followed by desiccated under vacuum.

2.4. Synthesis of polymer anchored oxovanadium(IV) catalyst, PS-VOnaph

1 g of polymer anchored PS-naph ligand (2) was stirred with 0.5 g of vanadyl acetylacetonate [38] in absolute ethanol (20 mL) at 70 °C for 24 h. After cooling it to nearly room temperature the complex was filtered and washed systematically with ethanol, dioxane and methanol successively to remove any unreacted metal ions. It was dried under vacuum. Finally the polymer bound oxovanadium catalyst (3) was obtained which was brown in color. The scheme for synthesizing polymer bound oxovanadium catalyst, PS-VO-naph, is represented in Scheme 1.



Scheme 1. Preparation of polystyrene anchored Oxovanadium(IV) catalyst.

2.5. Methods of oxidation reaction catalyzed by PS-VO-naph catalyst

2.5.1. For aromatic alkane oxidation

A mixture of 5.0 mmol of aromatic alkane, 30% aqueous H_2O_2 (15.0 mmol), acetonitrile (10 mL) and 30 mg of oxovanadium(IV) catalyst was placed in a 100 mL two-necked round-bottomed flask. The representative reaction mixture was stirred at 65 °C upto 6 h.

2.5.2. For aromatic alkene oxidation

Additionally another reaction mixture was set up by covering 5.0 mmol of aromatic alkene, 30% aqueous H_2O_2 (15.0 mmol), acetonitrile (10 mL) and 30 mg of oxovanadium(IV) catalyst in a 100 mL two-necked round-bottomed flask with stirring at 60 °C for 6 h.

In both the experiments the oxidant, 30% aqueous H_2O_2 was added dropwise maintaining a definite time interval. The Gas chromatographic analysis was performed for each aromatic alkanes and alkenes separately. GC technique was used to record the progress of oxidation reaction by collecting the ultimate reaction mixtures at various time interims. After the end of reaction, the mixture was cooled and filtered to separate out the involved catalyst from the medium. Then the filtrate was passed through anhydrous Na_2SO_4 to dehydrate the organic layer. After that the remaining reaction mixture was analyzed through GC technique using biphenyl for aromatic alkane oxidation and dodecane for aromatic alkene oxidation reaction as internal standard respectively. The corresponding oxidized products of aromatic alkanes and alkenes were detected by comparing the chromatograms with the respective authentic samples (Figs. S1–S11; supplementary file).

3. Results and discussion

3.1. Characterization of polymer attached ligand and oxovanadium complex

The polymer anchored ligand (PS-naph) and the oxovanadium catalyst (PS-VO-naph) have been systematically analyzed with FT-IR and UV–Visible spectroscopy, scanning electron microscopy (SEM) and

Table 1

Assignment (of the	chemical	composition	of p	olymer	supported	ligand	and	its
oxovanadiun	n comp	olex.							

Compound	Colour	C%	H%	N%	Metal%	Nitrogen:Metal
PS-naph	Green	76.14	4.31	11.28	-	4.11:1
PS-VO-naph	Brown	66.73	4.05	7.43	6.58	

thermo gravimetric analysis (TGA) together with elemental analysis, powder XRD, TEM and surface area measurement.

3.1.1. Elemental analysis

The elemental analysis of the polymer grafted ligand and oxovanadium(IV) catalyst are expressed in Table 1. It reveals that the nitrogen to metal ratio in the oxovanadium(IV) catalyst is nearly 4.11:1. Atomic absorption spectroscopy (AAS) measures the 6.58 wt% metal loading on the catalyst (PS-VO-naph) positively.

3.1.2. FT-IR spectroscopic studies

The FT-IR bands of polymer grafted ligand (PS-naph) and catalyst (PS-VO-naph) are depicted in Fig. 1. In the polymer supported ligand, the broad absorption band at 3412 cm^{-1} corroborates the vibrational frequency of the naphtholic –OH existing in the material. The sharp aromatic vibration of C–H bonds came out at 3024 and 2919 cm⁻¹ for the azo ligand. In the ligand, PS-naph, the characteristic peak around 1492–1452 cm⁻¹ describes that azo (N=N) group is attached with the naphthyl moiety [39]. The catalyst shows the N=N stretching at slight lower frequency in the range $1491-1449 \text{ cm}^{-1}$, which ascribes the -N=N- group bonded to vanadium metal site. In the ligand, the peak at 1369 cm⁻¹ directs the vibrational frequency of C–O stretching (while not connected to vanadium) is shifted to 1364 cm^{-1} after complex formation with vanadium in the PS-VO-naph. The polystyrene embedded oxovanadium complex revealed a discrete peak near at 537 cm⁻¹ signifying the V-N bond [40]. The corresponding frequencies appeared at 461 cm^{-1} for V–O bond [40] and 965 cm^{-1} due to stretching vibration of V=O bond respectively [41].

3.1.3. UV-Visible spectroscopic investigations

The absorption bands of the PS-naph ligand and its oxovanadium complex have been recorded (Fig. 2). The characteristic absorption in the range 295–348 nm is assigned to the π - π^* (intramolecular charge transfer) of the naphthalene ring and $n-\pi^*$ electronic transition for azo group (-N=N-) attached to the ligand (PS-naph). The spectral band observed for azo group in the PS-naph ligand is shifted to higher intensity band of 355 nm in the vanadium catalyst. Such shift in the absorption value represents an attachment of the vanadium metal to the -N=N- group of the polymer anchored ligand. The absorption bands in the 368–389 nm region substantiates the $n-\pi^*$ electronic transition of the non-bonding electrons residing on N-atom of the arylazo group contained in oxovanadium catalyst. The appearance of the broad shoulder close to 575-580 nm (Fig. 2, inset) corresponds to the weak dd electronic transition occurring in the vanadium containing complex. The band appears in the UV absorption region near 360 nm attributed to the LMCT from HOMO of PS-naph ligand to the LUMO of vanadium metal exists in the catalyst (PS-VO-naph) [Fig. 2, inset] [42].

3.1.4. Microscopic analysis

3.1.4.1. SEM analysis. The scanning electron microscopic (SEM) pictures of the polymer attached azo ligand (PS-naph) (A) and its oxovanadium complex (PS-VO-naph) (B) are given in Fig. 3. From the recorded SEM images it was realized that structural alterations occurred on the polystyrene beads. The SEM image corresponds to the polymer bound azo ligand depicts the perfectly smoothening of its surface. However the SEM structure of the metal bound catalyst represents the attachment of some irregular particles agglomerated at the polymer



Fig. 1. FT-IR bands of (A) polymer anchored ligand PS-naph and (B) PS-VO-naph catalyst.



Fig. 2. UV–Vis spectra of (A) polymer anchored ligand PS-naph and (B) PS-VO-naph catalyst.

surface. This creates a roughening of the smooth polymeric matrix.

Energy dispersive spectroscopic exploration of X-rays (EDAX) for the polymer anchored catalyst clearly shows the presence of vanadium metal content as observed in the spectra (Fig. 4). It is quite rational to realize the progress of the polymer anchored vanadium complex formation with the azo ligand from the following EDAX spectral analysis. The combination of SEM-EDAX analysis supports to confirm the attachment of vanadium metal into the polymer tagged azo ligand. This also suggests the loading of vanadium metal on the polymer surface.

3.1.4.2. TEM analysis. The ultra high resolution transmission electron microscopy (UHR-TEM) images of polymer grafted PS-naph ligand and PS-VO-naph catalyst are demonstrated in Fig. As observed from Fig. 5A and B for the ligand and Fig. 5C and 5D for the catalyst, the lattice fringes are absent in the bright field TEM images which suggests that both of the ligand and catalyst are amorphous in nature. This fact is also

confirmed by the lack of intense XRD peaks in the materials. This could be attributed due to the non-crystalline or amorphous nature of the materials. The contrast of the images is mass thickness contrast which was altered sharply with a absolute change in morphology in the image of PS-VO-naph catalyst [43]. The UHR-TEM image was taken for the catalyst providing additional information about the overlapping of some mass content on the polymeric matrix [Fig. 5C and D]. The EDAX spectra confirm the presence of vanadium in the studied sample of PS-VO-naph catalyst. The SAED pattern of polymer grafted PS-VO-naph catalyst is represented in Fig. 5E.

3.1.5. Thermal analysis

The TGA profile diagram of the polymer attached azo ligand (PS-naph) and its oxovanadium complex (PS-VO-naph) were marked at 12.00 °C/min temperature rate under N₂ flow to recognize the thermal steadiness of the materials. The TGA plot of the material is represented with a range of 30–600 °C (Fig. 6). The polymer anchored azo ligand dropped its weight in 275–435 °C whereas the oxovanadium complex at 280–450 °C. Hence from the comparison of stability of both the materials, it can be concluded that polymer bound metal catalyst possesses slightly higher thermal stability than the corresponding ligand only. From the differential thermal analysis (DTA) of the materials, PS-naph and PS-VO-naph (Fig. 6), it can be concluded that both the materials were decomposed through an endothermic reaction approach.

3.1.6. Powder X-ray diffraction analysis

The wide angle powder X-ray diffraction patterns of the polymer bound PS-naph ligand, PS-VO-naph catalyst and the reused catalyst are represented in Fig. 7. The characteristic XRD patterns of these materials are almost identical in nature. The XRD pattern displays a broad band for 20 in the range of 15-25°. Appearance of no sharp distinct peak in the wide angle PXRD patterns symbolizes the non crystalline nature of the PS-VO-naph catalyst as well as reused catalyst. This feature indicates the amorphous character, *i.e.*, there was no crystalline structural feature visualized in the prepared materials [44].

3.1.7. Surface area measurement

3.1.7.1. BET analysis of catalyst. The characteristic and precise N_2 sorption analysis was executed to determine the specific surface area of PS-VO-naph catalyst at 77 K temperature in the presence of nitrogen



Fig. 3. SEM images of (A) polymer anchored ligand PS-naph and (B) PS-VO-naph catalyst.

gas as adsorbate molecule after outgassing the sample for 12 h at 413 K. The N₂ adsorption/desorption isotherm of PS-VO-naph sample is shown in Fig. 8. The BET (Brunauer-Emmett-Teller) surface area of PS-VO-naph material was $25.4 \text{ m}^2 \text{ g}^{-1}$, as determined with the help of the plot. The pore size distribution curve has been drawn with the help of NLDFT (non-local distribution functional theory) method and is represented in Fig. B. The De Boer statistical thickness (*t*-plot) illustrates that the total BET surface area of the PS-VO-naph material is only $25.4 \text{ m}^2 \text{ g}^{-1}$, due to the amorphous nature of the catalyst containing the polystyrene polymer.

3.2. Interpretation of catalytic activities

3.2.1. Oxidation of aromatic alkanes with H_2O_2 catalyzed by PS-VO-naph The heterogeneous PS-VO-naph catalyst played an excellent catalytic activity in the oxidation of aromatic alkanes and alkenes with 30% aqueous H_2O_2 as a non-hazardous oxidant. The catalytic oxidation of aromatic alkanes was investigated with methyl benzene as a model aromatic alkane (Scheme 2). The measurable reaction parameters were accurately optimized by variation of several oxidants, solvents, toluene to H_2O_2 molar ratio, temperature, amount of vanadium loading and along with the effect of catalytic surface area.

3.2.2. Effect of several oxidants

The oxidation of toluene was performed with different oxidants, such as NaIO₄, 30% aq·H₂O₂, O₂ (1 atm.), and TBHP (70% aq.) to optimize the suitable oxidant. The corresponding product selectivity and conversion to benzaldehyde are highlighted in Table 2. In absence of oxidant the catalytic oxidation reaction did not run, although the catalyst PS-VO-naph was employed in the reaction (Table 2, entry 1). When NaIO₄ and 70% aq. TBHP were used as oxidant the conversion of the substrate were obtained as 34% and 59% respectively. Whereas the benzaldehyde selectivity was 55% and 68% respectively (Table 2, entries 2 and 4). Molecular O₂ (1 atm.) was inert towards this reaction (Table 2, entry 3). In presence of 30% aq H_2O_2 , the highest conversion of toluene was 79% of and the benzaldehyde selectivity was obtained as 87% (Table 2, entry 5). However without PS-VO-naph catalyst in the medium, no progress of reaction was monitored (Table 2, entry 6). Consequently 30% aq H_2O_2 may be preferred as suitable oxidizing agent for oxidation of toluene derivatives.

3.2.3. Effect of solvents

A variety of solvents like acetonitrile, dichloromethane, ethanol, DMF, and H_2O were used to determine the suitable and optimized solvent for toluene oxidation reaction and the corresponding observations are depicted in Fig. 9. Using acetonitrile as the solvent, a maximum of 79% conversion and 87% of benzaldehyde selectivity were found. The conversion and selectivity of product were gradually decreased on moving from dichloromethane to ethanol and then DMF, while contribution of water was negligible (Fig. 9).

3.2.4. Effect of H_2O_2 molar ratio

The concentration of H_2O_2 in the oxidation is a significant parameter affecting the toluene oxidation process. In this perspective we have examined the influence of molar ratio of toluene: H_2O_2 and results are shown in Fig. 10. The toluene oxidation was conducted with 1:1, 1:2, 1:3 and 1:4 M ratio of toluene to 30% aq H_2O_2 respectively to monitor whether the oxidation process was influenced by the concentration of substrate and oxidant (Fig. 10). The maximum toluene conversion was recorded as 79% which leads to the 87% of benzaldehyde selectivity in presence of 1:3 M ratio of the substrate to oxidant. During the oxidation process, addition of substrate to oxidant in 1:4 M



Fig. 4. EDAX of (A) polymer anchored ligand PS-naph and (B) PS-VO-naph catalyst.



Fig. 5. The UHR-TEM images of PS-naph at two different magnifications: 100 nm (A) and 50 nm (B); and of PS-VO-naph at two different magnifications: 100 nm (C) and 50 nm (D). The SAED pattern of PS-VO-naph catalyst (E).

ratio exhibited an abrupt fall in benzaldehyde selectivity. In some of earlier reported work, it was observed that with increase in the molar ratio of toluene: H_2O_2 , the conversion of toluene gradually decreased while the change in selectivity did not follow a regular trend [3]. In fact when toluene: H_2O_2 molar ratio was adjusted to 1:3, the conversion of toluene was 79% with the benzaldehyde selectivity of 87%. However, when the toluene: H_2O_2 molar ratio increased to 1:4, the toluene conversion increased to just 81% whereas the selectivity of benzaldehyde was decreased to 65%. In another report, toluene conversion was observed to be increased with rise in the toluene: H_2O_2 molar ratio but the selectivity of benzaldehyde was found to be decreased slightly [45].

The enhancement in molar ratio of H₂O₂, accelerated the oxidation

of the side chain, hence the toluene conversion increased accordingly. But the selectivity of benzaldehyde was decreased in presence of excess of H_2O_2 concentration. Surprisingly, using toluene: H_2O_2 molar ratio as 1:4, the benzaldehyde selectivity was started to decrease. This suggests that higher the stoichiometric amount of H_2O_2 was utilized during oxidation, the higher degree of thermal decomposition of H_2O_2 occurred, consequence to the small increment in toluene conversion as well as reduction in benzaldehyde selectivity. Therefore, the optimal molar ratio of toluene to H_2O_2 was 1:3 [13b]. One of the possible contributions for the decrease in selectivity is probably due to the formation of the over-oxidized products if any. The conversion factor did not improve rapidly (from 79% to 81%), as the reactant molecules



Fig. 6. (a) TGA plot of polymer anchored ligand PS-naph and PS-VO-naph catalyst; (b) DTA plot: (A) polymer anchored ligand PS-naph and (B) PS-VO-naph catalyst.

might be restricted to appear in close vicinity of the catalyst through water formation in the reaction medium by the decomposition of H_2O_2 [46].

3.2.5. Effect of reaction temperature

The activity of the catalyst for toluene oxidation with varying temperature has been outlined in Fig. 11. The selectivity of benzaldehyde was gradually decreased with rise in the temperature upto 85 °C, on account of the decomposition of H₂O₂ and probably due to the formation of uncontrolled oxidized product e.g. benzoic acid. We believe that due to the presence of vanadium species in the catalytic system, the self decomposition of H2O2 was restricted to higher temperature [46]. At lower temperature, a slight conversion of toluene was achieved while the selectivity of benzaldehyde was observed high but with increasing temperature, the toluene conversion increases significantly (Fig. 11). The selectivity of benzaldehyde was decreased to some extent because of formation of benzoic acid with increasing temperature correspondingly. Some earlier report reveals that in presence of CuCr₂O₄ nanoparticles catalyst, the conversion of toluene was found to be increased with rise in reaction temperature [2]. Another reported work shows that with increment of reaction temperature, the conversion of toluene was found to be increased whereas the selectivity of benzaldehyde was found to follow a decreasing order [45]. Oxidation leads to the highest toluene conversion (79%) and a slight lower selectivity (87%) of benzaldehyde at 65 °C temperature compared to the lower temperature region. Now, if the reaction temperature was raised from 65 °C, the toluene conversion remains almost unchanged; on the contrary the benzaldehyde selectivity was decreased at a greater extent. While the reaction was subjected to the higher temperature greater than 65 °C, the presence of other oxidized products in minute amounts with

benzaldehyde may be the another reason for decreased selectivity of benzaldehyde in the reaction mixture [2].

3.2.6. Effect of amount of catalyst

The quantity of catalyst was varied from 10 mg to 50 mg for the reaction to optimize the PS-VO-naph catalytic amount and the corresponding outcomes are indicated in Fig. 12. An increment of the catalyst quantity from 10 mg to 30 mg, the toluene conversion improves to such extent but further rise in catalyst amount the selectivity of benzaldehyde was dropped. In that context the conversion of toluene was remain almost unaltered (Fig. 12).

3.2.7. Effect of vanadium metal loading

The influence of the vanadium metal loading on the catalytic oxidation reaction of toluene has been studied by varying the vanadium metal loading (5.0-8.0 wt% of V) on the polymer grafted catalyst and the corresponding results are shown in Table 3. It is observed that with increasing the metal loading, the conversion of toluene was also increased. From this standpoint, the observed higher catalytic activity in the relatively lower vanadium loading (5.0-6.58 wt% of V) could be attributed to the fact that vanadium species comprising the active sites in the catalyst responsible for toluene oxidation. The initial increase of catalytic activity with the vanadium content, upto 6.58 wt% may because of the monolayer loading. But after a certain higher range of vanadium loading (6.58 wt% of V), the conversion of toluene in terms of TON was dropped slightly. The rise in the vanadium loading above monolayer coverage switches the formation of multilayer segment as a consequence to the decrease in toluene conversion. Further enrichment with vanadium wt% reduces the conversion of toluene gradually which may be attributed to the appearing of reasonably less active sites on top



Fig. 7. The wide angle powder XRD pattern of (A) polymer anchored ligand PS-naph, (B) PS-VO-naph catalyst and (C) reused catalyst.



Fig. 8. N2 adsorption/desorption isotherms of PS-VO-naph catalyst (A); Pore size distribution Plot (B).



Scheme 2. Oxidation of toluene in presence of PS-VO-naph catalyst.

Table 2 Optimization of oxidant and catalyst for the oxidation of toluene.^a

Entry	Catalyst	Oxidant	Conversion(%) ^b	Selectivity of benzaldehyde (%) ^b
1	PS-VO-naph	No	No reaction	No reaction
2	PS-VO-naph	NaIO ₄	34	55
3	PS-VO-naph	O2 (1 atm.)	No reaction	No reaction
4	PS-VO-naph	70% aq. TBHP	59	68
5 ^c	PS-VO-naph	30% aq∙H₂O₂	79	87
6 ^c	Nil	30% aq·H ₂ O ₂	No reaction	No reaction

 $^{\rm a}$ Reaction conditions: toluene (5.0 mmol), acetonitrile (10 mL), oxidant (15.0 mmol), catalyst (30 mg, 6.58 wt% Vanadium loading), temperature 65 °C, time 6 h.

^b Determined by GC.

^c H₂O₂ (30% aq.) was added maintaining a definite time interval.

of the multilayer portions and their lower surface concentration [47].

3.2.8. Effect of catalytic surface area

The catalytic efficiency of the polymer supported vanadium catalyst was compared with the different reported heterogeneous catalyst to realize the influence of surface area of PS-VO-naph on the selectivity of product throughout the toluene oxidation process. It is clearly seen from the Table 4 that the polymer supported catalyst exhibited significantly higher toluene conversion (79%) in contrast to that reported other heterogeneous materials [3,25b]. In line with the conversion factor a higher selectivity (87%) of the oxidized product of toluene was observed when polystyrene supported VO-naph catalyst was applied. The result signifies that the surface of the polystyrene anchored vanadium complex has definite contribution to the toluene conversion as well as selectivity of the benzaldehyde. From the comparative analysis of BET surface area on Table 4, it was observed that the surface area of PS-VO-naph catalyst contributed the activity of the catalyst as well as selectivity during toluene oxidation.



Fig. 9. Dependence of solvent on PS-VO-naph catalyzed toluene oxidation. Reaction conditions: toluene (5.0 mmol), solvent (10 mL), 30% aqH_2O_2 (15.0 mmol), catalyst (30 mg, 6.58 wt% Vanadium loading), temperature 65 °C, time 6 h.



Fig. 10. Effect of toluene: $\rm H_2O_2$ molar ratio during PS-VO-naph catalyzed oxidation of toluene. Reaction conditions: toluene (5.0 mmol), acetonitrile (10 mL), 30% aq-H_2O_2, catalyst (30 mg, 6.58 wt% Vanadium loading), temperature 65 °C, time 6 h.

3.2.9. Catalytic oxidation of different aromatic alkanes

The exact optimized condition for toluene oxidation was examined using 30% aqH_2O_2 (as the best oxidant) in presence of 30 mg of PS-VO-



Fig. 11. Temperature effect on oxidation of toluene catalyzed by PS-VO-naph complex. Reaction conditions: toluene (5.0 mmol), acetonitrile (10 mL), 30% aqH_2O_2 (15.0 mmol), catalyst (30 mg, 6.58 wt% Vanadium loading), time 6 h.



Fig. 12. Effect of PS-VO-naph catalyst amount on oxidation of toluene by H_2O_2 . Reaction conditions: toluene (5.0 mmol), acetonitrile (10 mL), 30% aq H_2O_2 (15.0 mmol), temperature 65 °C, time 6 h.

Optimization of the amount of vanadium metal loading for the oxidation of toluene. $^{\rm a}$

Entry	Vanadium metal loading (wt%)	Conversion(%) ^b	TON
1	5.0	69.5	90
2	5.5	72.3	93
3	6.5	75.3	97
4	6.58	79	102
5	7.5	65	84
6	8.0	61.2	79

 a Reaction conditions: toluene (5.0 mmol), acetonitrile (10 mL), 30% aq:H_2O_2 (15.0 mmol), catalyst, temperature 65 °C, time 6 h.

^b Determined by GC.

naph catalyst in acetonitrile for 6 h at 65 °C temperature. These optimized reaction conditions for selective oxidation of toluene to benzaldehyde were extended to the other substituted aromatic alkanes (Table 5). As obvious from Table 5, the electron donating $-CH_3$ group attached to o-xylene, p-xylene and m-xylene experienced the higher viz 88%, 85% and 82% conversion with respect to the substrate committing up to 91%, 93% and 94% selectivity of the corresponding benzaldehydes (entries 2–4, Table 5). Mesitylene contributed 86% conversion and 92% selectivity of 3,5-dimethyl benzaldehyde (Table 5, entry 5). The electron-withdrawing factor was realized for -Cl and $-NO_2$ substituted toluenes (Table 5, entries 6–7) with 56% and 23% conversion respectively while the selectivity of 4-chloro benzaldehyde and 2-nitro benzaldehyde were 85% and 91% respectively. Additionally, the electron-donating effect of $-OCH_3$ in toluene molecule brought about up to 92% conversion and 64% selectivity of 4methoxy benaldehyde (Table 5, entry 8). Ethyl benzene contributed almost 96% conversion and the selectivity of the resultant acetophenone was 95% (Table 5, entry 9). The highest H₂O₂ efficiency of 30.4% was observed for ethyl benzene (Table 5, entry 9) and the lowest efficiency *i.e.* 7% was observed for 2-nitro toluene (Table 5, entry 7) [46].

3.2.10. PS-VO-naph catalyzed oxidation of aromatic alkenes by H_2O_2

For the typical catalytic oxidation of aromatic alkenes we choose styrene for model substrate (Scheme 3). The different reaction variables such as: oxidant, solvents, styrene to H_2O_2 molar concentration ratio, temperature, amount of vanadium metal loading and the effect of catalytic surface area were varied to optimize the process.

3.2.11. Effect of several oxidants

We have investigated the suitable oxidant competent for the oxidation of styrene, out of the different oxidants like NaIO₄, 30% aq·H₂O₂, O₂ (1 atm.), 70% aq. TBHP. Throughout the optimization, it was identified that in absence of any oxidant no conversion of styrene was experienced (Table 6, entry 1) irrespective of the presence of PS-VO-naph catalyst in the medium. The greater conversion of styrene *i.e.* 97% with 88% selectivity of benzaldehyde was detected in presence of 30% aq·H₂O₂ (Table 6, entry 2). When 70% aq. TBHP and NaIO₄ were used as oxidant (Table 6, entries 3–4), the conversion as well as selectivity was found smaller than that of 30% aq·H₂O₂. In presence of O₂ (1 atm.) very low conversion was observed (Table 6, entry 5). Conversely, when 30% aqueous H₂O₂ was treated with the reaction in absence of catalyst, a remarkably poor conversion was detected (Table 6, entry 6).

3.2.12. Effect of solvents

The styrene oxidation was treated with a number of polar solvents and the corresponding conversion of substrate and selectivity of benzaldehyde are shown in Fig. 13. Acetonitrile as a solvent accomplished a maximum of 97% styrene conversion with 88% selectivity of benzaldehyde.

3.2.13. Effect of styrene: H_2O_2 molar ratio

The oxidation of the model substrate styrene was performed successively with 1:1, 1:2, 1:3 and 1:4 M concentration ratio of styrene to oxidant (30% aqH₂O₂) for defining the best substrate to oxidant molar ratio (Fig. 14). It indicates that in presence of styrene:oxidant in 1:3 M ratio, 97% styrene conversion were obtained, providing 88% selectivity of benzaldehyde after reaction completion. Later increase in oxidant concentration, the selectivity of aromatic aldehyde was considerably reduced.

3.2.14. Effect of reaction temperature

Variable temperature (from 40 to 70 °C) experiments were conducted for the progress of styrene oxidation to optimize the exact temperature required as shown in Fig. 15. The diagram clearly shows that the conversion and selectivity factor is increased gradually with temperature enhancement. At 60 °C temperature, a maximum of 97% styrene conversion was reached however the selectivity of benzaldehyde was found 88%. Further raise in temperature the benzaldehyde selectivity was dropped at a larger extent.

3.2.15. Effect of amount of catalyst

The studied oxidation was executed with different quantity of catalyst to optimize exact amount of catalyst compulsory for the procedure (Fig. 16). The styrene conversion was improved progressively by consuming up to 30 mg of catalyst, even though the selectivity of benzaldehyde was remained almost same. Subsequent increasing the amount of PS-VO-naph catalyst, both the conversion and selectivity were reduced gradually.

Effect of surface area on the activity as well as selectivity of the catalyst for the oxidation of toluene.

Entry	Complex	Surface area ($m^2 g^{-1}$)	Conversion (%) ^e	Selectivity of benzaldehyde (%) $^{\rm e}$	[Ref.]
1 ^a	PS-naph	20.2	Trace	-	Present work
2 ^a	PS-VO-naph	25.4	79	87	Present work
3 ^b	KIT-6	493	0.14	^{>} 99.9	[3a]
4 ^b	KIT-6-VPO	150	17.76	69.24	[3a]
5 [°]	Cu-NZ	512.64	95.4	34.07	[3b]
6 ^c	Cu-MZ	432.89	85.7	47.61	[3b]
7 ^d	Fe ₂ O ₃ /HZSM-5	303.5	17.3	51.4	[26a]
8 ^d	Fe ₂ O ₃ /HY	471.1	5.7	88.9	[26a]

Reaction conditions:

^a Toluene (5.0 mmol), acetonitrile (10 mL), 30% aq·H₂O₂ (15.0 mmol), complex (30 mg), temperature 65 °C, time 6 h.

^b Toluene (3.5 mL), acetonitrile (10 mL), toluene: H_2O_2 mole ratio = 1:1.4, complex (0.1 g), temperature 75 °C, time 10 h.

^c Toluene (25 mL), catalyst (1.0 g), 25 mL of 30 wt% H₂O₂ with 25 mL deionized water, pressure 5.0 bar (with N₂ gas), temperature 180 °C, time 4 h.

 d Toluene (5 mL), molar ratio of H₂O₂ to toluene = 3:1, solvent-free condition, catalyst (0.4 g), temperature 90 °C, time 4 h.

^e Determined by GC.

Table 5

Catalytic oxidation of aromatic alkanes by 30% aq·H₂O₂ using PS-VO-naph catalyst.^a

Entry	Substrate	Product	Conversion (%) ^b	Selectivity (%) ^b	TON	H ₂ O ₂ efficiency (%)
1	CH ₃	0	79	87	102	23.0
2	CH ₃ CH ₃	CH ₃	88	91	114	26.7
3	CH ₃		85	93	110	26.4
4	H ₃ C CH ₃	H ₃ C 0	82	94	106	25.7
5	CH ₃	CH ₃	86	92	111	26.4
	H ₃ C CH ₃	H.C. CH.				
6	CH ₃		56	85	72	15.9
7	CI NO ₂ CH ₃		23	91	30	7.0
8	CH ₃		92	64	119	19.6
9	H ₃ CO H H	H ₃ CO CH ₃	96	95	124	30.4
	CH ₃					

^a Reaction conditions: substrate (5.0 mmol), acetonitrile (10 mL), 30% aq H_2O_2 (15.0 mmol), catalyst (30 mg, 6.58 wt% Vanadium loading), temperature 65 °C, time 6 h.

 $^{\rm b}$ Determined by GC·H_2O_2 efficiency = [moles of selective product formed/total moles of H_2O_2 added] \times 100.



Scheme 3. Oxidation of styrene in presence of PS-VO-naph catalyst.

3.2.16. Effect of vanadium metal loading

The catalytic oxidation reaction of styrene to benzaldehyde was also influenced by the wt % of vanadium loading in the polymer grafted catalyst. In order to analyze the effect of metal loading, the conversion of styrene was recorded by varying the vanadium wt% from 5.0 to 8.0 and the results are shown in Table 7. It was detected that the conversion of styrene was increased with increasing the vanadium loading. In

Optimization of oxidant and catalyst for the oxidation of styrene.^a

Entry	Catalyst	Oxidant	Conversion(%) ^b	Selectivity of benzaldehyde(%) ^b
1	PS-VO-naph	No	No reaction	No reaction
2 ^c	PS-VO-naph	30%	97	88
		aq·H ₂ O ₂		
3	PS-VO-naph	70% aq. TBHP	56	81
4	PS-VO-naph	NaIO ₄	36	48
5	PS-VO-naph	O2 (1 atm.)	~4	69
6 ^c	No	30%	~7	71
		$aq H_2O_2$		

 $^{\rm a}$ Reaction conditions: styrene (5.0 mmol), acetonitrile (10 mL), oxidant (15.0 mmol), catalyst (30 mg, 6.58 wt% Vanadium loading), temperature 60 °C, time 6 h.

^b Determined by GC.

 $^{c}\,$ H2O2 (30% aq.) was added maintaining a definite time interval.



Fig. 13. Effect of solvent on PS-VO-naph catalyzed oxidation of styrene. Reaction conditions: styrene (5.0 mmol), solvent (10 mL), 30% aqH_2O_2 (15.0 mmol), catalyst (30 mg, 6.58 wt% Vanadium loading), temperature 60 °C, time 6 h.



Fig. 14. Effect of molar ratio (styrene: H_2O_2) on PS-VO-naph catalyzed oxidation of styrene. Reaction conditions: styrene (5.0 mmol), acetonitrile (10 mL), 30% aq H_2O_2 , catalyst (30 mg, 6.58 wt% Vanadium loading), temperature 60 °C, time 6 h.

relatively lower vanadium content (5.0–6.58 wt% of V), the higher catalytic activity was observed as depicted in Table 7. But after a certain range of loading (6.58 wt% of V) the conversion of styrene in terms



Fig. 15. Temperature effect on PS-VO-naph catalyzed oxidation of styrene. Reaction conditions: styrene (5.0 mmol), acetonitrile (10 mL), 30% aqH_2O_2 (15.0 mmol), catalyst (30 mg, 6.58 wt% Vanadium loading), time 6 h.



Fig. 16. Effect of catalyst (PS-VO-naph) amount on hydrogen peroxide oxidation of styrene. Reaction conditions: styrene (5.0 mmol), acetonitrile (10 mL), 30% aqH_2O_2 (15.0 mmol), temperature 60 °C, time 6 h.

Table 7

Optimization of the amount of vanadium metal loading for the oxidation of styrene. $^{\rm a}$

2			
Entry	Vanadium metal loading (wt%)	Conversion (%) ^b	TON
1	5.0	81	105
2	5.5	86.4	112
3	6.5	93.2	120
4	6.58	97	125
5	7.5	80	103
6	8.0	77	99

 a Reaction conditions: styrene (5.0 mmol), acetonitrile (10 mL), 30% aq:H_2O_2 (15.0 mmol), catalyst, temperature 60 °C, time 6 h.

^b Determined by GC.

of TON was dropped slightly. This may be attributed to the fact that vanadium loading upto 6.58 wt%, the monolayer formation (acts as active sites) is responsible for styrene oxidation. Indeed loading of higher wt% of vanadium in the PS-VO-naph, the monolayer formation then converts into the less active site on top of the multilayer portion, as a result of which conversion of styrene gets reduced [47].

3.2.17. Effect of catalytic surface area

The similar experiment was executed to detect the catalytic activity and the influence of surface area of PS-VO-naph catalyst during the styrene oxidation process. Herein we have reported (Table 8) that the polymer supported vanadium catalyst exhibited quite higher styrene

temperature for 6 h. By maintaining the optimized factors the similar

conditions were applied for the oxidation reactions of aromatic alkenes

(Table 9). Oxidation of styrene conversion up to 97% produced the

benzaldehyde with 88% selectivity (Table 9, entry 1). On the other

hand the catalytic oxidation of aliphatic alkene e.g. cyclohexene (84%

conversion) undergoes oxidation to 2-cyclohexene-1-one with 66% se-

lectivity (Table 9, entry 2). The substrate trans-stilbene was oxidized upto a conversion of 67% with 79% benzaldehyde selectivity (Table 9,

entry 3). 4-methyl benzaldehyde was produced with 85% conversion

and 86% selectivity from the substrate 4-methyl styrene having electron-releasing $-CH_3$ group (Table 9, entry 4). Styrene containing electron-attracting -Cl and $-NO_2$ groups, (Table 9, entry 5–6) provided

the respective benzaldehyde products with 87% and 82% selectivity.

The efficiency of H₂O₂ was highest (28.5%) for styrene oxidation

(Table 9, entry 1) while it was examined as lowest 17.6%, in case of

Entry	Complex	Surface area	Conversion (%) ^e	Selectivity of benzaldehyde (%) $^{\rm e}$	[Ref.]
1^{a}	PS-naph	$20.2 \mathrm{m}^2 \mathrm{g}^{-1}$	11	63	Present work
2 ^a	PS-VO-naph	$25.4 \mathrm{m^2 g^{-1}}$	97	88	Present work
3 ^b	Co ₃ O ₄ @HZSM-5	$329 \mathrm{cm}^2 \mathrm{g}^{-1}$	96.8	81.5	[7b]
4 ^c	PS-[Cu(Hfsal-aepy)Cl]	$16.47 \mathrm{m^2 g^{-1}}$	87.3	15.7	[10c]
5 [°]	PS-[Mn(Hfsal-aepy)Cl]	$15.68 \text{ m}^2 \text{ g}^{-1}$	75.4	21.3	[10c]
6 ^d	Mn-MIL-100	$1133 \text{ m}^2 \text{ g}^{-1}$	88.99	84.97	[25b]

Effect of surface area on the activity as well as selectivity of different catalyst for the oxidation of styrene.

Reaction conditions:

^a Styrene (5.0 mmol), acetonitrile (10 mL), 30% aq·H₂O₂ (15.0 mmol), complex (30 mg), temperature 60 °C, time 6 h.

^b Styrene (15 mmol), acetonitrile (16 mL), $Co_3O_4@$ HZSM-5 (0.1 g), H_2O_2 (75 mmol), 75 °C, 10 h.

 $^{\rm c}\,$ Styrene to TBHP mole ratio of 1:3, catalyst (25 mg), temperature 70 $^{\circ}\text{C}.$

^d Mn-MIL-100 (5 wt%), 3:1 M ratio of 70% TBHP/styrene, acetonitrile (1 mL), temperature 70 °C, time 10 h.

^e Determined by GC.

conversion (97%) in comparison to that of other reported heterogeneous catalyst. Again the selectivity of the styrene oxidized product was moderately enhanced (88%) in presence of PS-VO-naph catalyst in comparison to the previously reported catalyst as represented in Table 8 [7b,10c,25b]. The result implies that the surface of the polystyrene supported vanadium complex has active contribution to the styrene conversion. From the similar type of comparative analysis with BET surface area (Table 8), it was noticed that the surface area of PS-VOnaph catalyst has potential impact on the activity of the catalyst as well as selectivity throughout styrene oxidation.

3.2.18. Catalytic oxidation of different aromatic alkenes

The best reaction condition was monitored in acetonitrile solvent after examining the optimization process during the course of oxidation with 30% $aq H_2O_2$ in presence of 30 mg PS-VO-naph catalyst at 60 °C

Table 9

Catalytic oxidation of aromatic alkenes by 30% aq·H₂O₂ using PS-VO-naph catalyst.^a

Entry	Substrate	Product	Conversion (%) ^b	Selectivity (%) $^{\rm b}$	TON	H_2O_2 efficiency (%)
1			97	88	125	28.5
2*	H H		84	66	108	18.5
3			67	79	86	17.6
4	H.C	H ₃ C	85	86	110	24.4
5			88	87	114	25.5
6	O ₂ N	0 ₂ N	83	82	107	22.7

* Note: Cyclohexene is an aliphatic alkene.

^a Reaction conditions: substrate (5.0 mmol), acetonitrile (10 mL), 30% aq·H₂O₂ (15.0 mmol), catalyst (30 mg, 6.58 wt% Vanadium loading), temperature 60 °C, time 6 h.

^b Determined by GCH_2O_2 efficiency = [moles of selective product formed/total moles of H_2O_2 added] \times 100.

Reaction	Catalyst	Reaction conditions	Conversion/Selectivity (%)	Ref.
Oxidation of toluene	MPAV ₂ /Nb ₂ O5	Toluene (10 mmol), catalyst (50 mg), TBHP (8 mmol), inert atm., RT, 14 h	22/76	[48]
	Vanadium phosphorus oxide functionalized KIT-6	Toluene (3.5 mL), Toluene:H ₂ O ₂ mole ratio (1:1.4), catalyst (0.1 g), 75 °C, 10 h	17.76/69.24	[3]
	CoSBA-15	Toluene (2.4 $ imes$ 10 ⁻³ mol), TBHP (0.98 mL), catalyst (0.010 g), 80 °C , 1 h	7.97/63.8	[49]
	V-Mo-Fe-O composite catalyst	Toluene (1.75 g), catalyst (0.2 g), H ₂ O ₂ (30 wt%), 80 °C, 30 min	40.3/84.5	[13b]
	Pd/ Bi ₂ WO ₆	Toluene (1 mL), catalyst (50 mg), $\lambda > 400$ nm, irradiation time: 5 h, oxygen balloon (1 atm)	3.42/ 90	[20]
	PS-VO-naph	Toluene (5.0 mmol), 30% aq.H ₂ O ₂ (15.0 mmol), catalyst (30 mg), 65 °C, 6 h	28/62	This study
Oxidation of styrene	PS-K[VO ₂ (fsal-ohyba)]	Styrene (10 mmol), H ₂ O ₂ (20 mmol), catalyst (0.040 g), 80 °C, 6 h	79.7/60.65	[34]
	MOF-74(Cu/Co)	Styrene (5 mL, 43.6 mmol), oxygen balloon, catalyst (50 mg, ca. 0.15 mmol), 80 °C, 20 h.	30.4/43	[28b]
	Zeolite Y encaged Ru(III) and Fe(III) complex	Styrene (25 mmol), catalyst (12.5 mg), H ₂ O ₂ (25 mmol), 353 K, 18 h	76.1/93.6	[4]
	Mn-MIL-100	Styrene (1 mmol), TBHP/ Styrene (3:1), catalyst (5 wt%), 70 °C , 10 h	89/85	[25b]
	ZSM-5(60) zeolite catalyst	Styrene (20 mmol), TBHP (30 mmol), catalyst (0.15 g), 65 °C, 6 h	45.3/87.2	[51]
	PS-VO-naph	Styrene (5.0 mmol), 30% aq H_2O_2 (15.0 mmol), catalyst (30 mg), 60 °C, 6 h	97/88	This study

trans-stilbene oxidation (Table 9, entry 3) [46].

3.2.19. Comparative investigation on catalytic activity with other reported systems

The efficiency of the polystyrene incorporated oxovanadium(IV) catalyst, (PS-VO-naph) towards the aromatic alkane/alkene oxidation was compared (Table 10) with the formerly reported works. The catalytic oxidation reaction of aromatic alkane (toluene) furnished 22% conversion of toluene with 76% selectivity of benzaldehyde in the presence of MPAV₂/Nb₂O₅ [48]. Another work represented the 17.76% toluene conversion with 69.24% selectivity of benzaldehvde in the presence of vanadium phosphorus oxide functionalized KIT-6 catalyst [3]. CoSBA-15 effectively performed 7.97% conversion of toluene oxidation with 63.8% benzaldehyde selectivity [49]. Using our oxovanadium(IV) catalyst 79% conversion of toluene with 87% selectivity of the desired product benzaldehyde was obtained. Maurya et al. established that catalytic oxidation reaction of aromatic alkene (styrene) in association with PS-K[VO2(fsal-ohyba)] catalyst produced the 79.7% conversion of styrene and 60.65% benzaldehyde selectivity [34]. In another work reports about 30.4% conversion of styrene with 43% benzaldehyde selectivity was achieved in presence of MOF-74(Cu/Co) catalyst, [28b]. Conversely the Zeolite Y encaged Ru(III) and Fe(III) complex were relatively much effective for the 76.1% of styrene conversion with 93.6% benzaldehyde selectivity [4]. Some more relevant works are included in the given Table 10. Therefore using our oxovanadium(IV) catalyst 97% conversion of styrene with 88% selectivity of the desired product benzaldehyde was obtained.

3.3. Test for heterogeneity

During the oxidation reaction the controlled reaction of toluene was performed to investigate the leaching of the active vanadium metal from the metal immobilized complex. The same test was also executed with styrene under controlled reaction condition. A typical hot filtration test was conducted for oxidation reactions of both toluene and styrene individually by maintaining suitable optimized condition. After 3 h from the commencement of the title oxidation reaction, the reaction mixture was settled for cooling for the two cases. Afterwards the catalyst was extracted from the medium by centrifugation process. Under similar reaction condition without catalyst the subsequent prolonged oxidation process was executed with toluene and styrene separately for additional 3 h. The conversion of toluene was almost the same after the first 3 h and the next 3 h of the reaction. Similar effect was observed for styrene oxidation. Hence oxidation reaction did not run in absence of the PS-VO-naph catalyst for both the substrate toluene and styrene respectively. After removing the catalyst from the reaction mixture no leaching or decomposition of the catalyst was visualized in the filtrate. Additionally, no trace of vanadium metal content in the filtrate was appeared from the AAS experiment, within the detection limit (< 5 ppm). This fact approves no significant leaching of metal ion from PS-VO-naph catalyst during aromatic alkane/alkene oxidations. From the above test we can certainly elucidate that the toluene and styrene oxidation took place with the PS-VO-naph catalyst which is heterogeneous by nature.

3.4. Recyclability of catalyst

A catalyst with heterogeneous environment is constantly predominating over a homogeneous catalyst due to its recyclability and separation from reaction system. Accordingly the recyclability of the PS-VO-naph catalyst was checked for the oxidation of both toluene and styrene by 30% aq·H₂O₂ oxidant (Fig. 17a). After the first run, the catalyst PS-VO-naph was easily withdrawn from the reaction system by centrifugation process. Subsequent washings with ethyl acetate and methanol were conducted to remove any unreacted materials present in the catalyst. Further it was desiccated under vacuum for the subsequent



Fig. 17. (a) Recycling efficiency of oxovanadium(IV) catalyst; (b) FT-IR spectra of reused oxovanadium(IV) catalyst.

reaction run. Fig. 17a shows that the present catalyst can be recycled up to six runs under the optimized reaction condition. There observed no leaching of metal and no abrupt change in the conversion of the substrates and selectivity of the oxygenated products in recycling experiments. From FT-IR spectroscopic studies it was observed that the FT-IR spectrum (Fig. 17b) of the reused vanadium catalyst was almost similar with the freshly prepared catalyst.

4. Conclusion

In summary, we have successfully outlined a polymer grafted heterogeneous oxovanadium naphthyl-azo catalyst (PS-VO-naph) for selective oxidation of aromatic alkanes and alkenes by an environmentfriendly oxidant, 30% aqH₂O₂ under ambient conditions. Hydrogen peroxide is an excellent oxidant throughout the oxidation process, since it delivers water as the only byproduct. The oxidation of the hydrocarbons deals with some industrially significant oxidized products among which benzaldehydes are the most promising owing to its large industrial importance. Out of the several aromatic alkanes investigated, ethyl benzene provided the maximum conversion of 96% with respect to substrate and maximum of 95% selectivity of the resulting carbonyl compound under optimized reaction conditions. The aromatic alkenes produced their corresponding carbonyl compounds which could undergo further catalytic oxidation process to provide the carboxylic acids at definite condition. These resulting compounds have greater significance in various industrial organic transformations. Styrene contributed the maximum conversion of 97% and 88% selectivity of benzaldehyde under optimized conditions. The corresponding oxygenated products were identified using gas chromatograph (GC). Our catalyst accomplished the excellent catalytic efficiency and activity for both aromatic alkanes and alkenes oxidation reactions. Furthermore, the complex did not exhibit any leaching of vanadium, which proves the heterogeneous activity of the catalyst. Additionally the complex is reusable up to maximum of six reaction cycles without substantial and abrupt modification in catalytic property during conversion of both toluene and styrene to the product benzaldehyde exclusively.

Acknowledgements

S.M.I. acknowledges Board of Research in Nuclear Sciences (BRNS), Project reference No: 37(2)/14/03/2018-BRNS/37003, Govt. of India and the Department of Science and Technology (DST-SERB, Project No. EMR/2016/004956), New Delhi, Govt. of India, for funding. PP acknowledges Aliah University, Kolkata for financial support. AG expresses his sincere gratitude to the SERB-NPDF, DST, New Delhi, India (File No. PDF/2017/000478) for the National Post-Doctoral Fellowship. SMI is also thankful to Council of Scientific and Industrial and Research, CSIR (project reference no 02(0284)2016/EMR-II dated 06/12/2016) New Delhi, Govt. of India and Department of Science and Technology, West Bengal (DST-WB, Sanction No. 811(sanc.)/ST/P/S&T/4G-8/2014 Dated: 04.01.2016) for providing financial support. SMI acknowledges University of Kalyani, India for providing personal research grant. We sincerely acknowledge the DST and UGC, New Delhi, Govt. of India, for providing grant under DST-FIST, DST-PURSE and UGC-SAP program to the Department of Chemistry, University of Kalyani. SMI acknowledges Dr. Ankur Bordoloi and Manideepa Sengupta of IIP Dehradun for their various supports for this research work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2019.04.037.

References

- [1] Z. Guo, B. Liu, Q. Zhang, W. Deng, Y. Wang, Y. Yang, Chem. Soc. Rev. 43 (2014) 3480–3524.
- [2] S.S. Acharyya, S. Ghosh, R. Tiwari, B. Sarkar, R.K. Singha, C. Pendem, T. Sasaki, R. Bal, Green Chem. 16 (2014) 2500–2508.
- [3] (a) M. Rezaei, A.N. Chermahini, H.A. Dabbagh, J. Environ. Chem. Eng. 5 (2017) 3529–3539;
- (b) N. Viswanadham, S.K. Saxena, A.H. Al-Muhtaseb, Mater. Today Chem. 3 (2017) 37–48.
- [4] D.R. Godhani, H.D. Nakum, D.K. Parmar, J.P. Mehta, N.C. Desai, J. Mol. Catal. A: Chem. 426 (2017) 223–237.
- [5] (a) A. Dali, I.R. Hammoumraoui, A.C. Braham, R. Bachir, RSC Adv. 5 (2015) 29167–29178;
- (b) M.-C. Hsiao, S.-T. Liu, Catal. Lett. 139 (2010) 61–66.
 [6] S.M. Islam, A.S. Roy, P. Mondal, N. Salam, J. Mol. Catal. A: Chem.
- [6] S.M. Islam, A.S. Roy, P. Mondal, N. Salam, J. Mol. Catal. A: Chem. 358 (2012) 38–48.
- [7] (a) H. Wang, H. Ruan, M. Feng, Y. Qin, H. Job, L. Luo, C. Wang, M.H. Engelhard,
 E. Kuhn, X. Chen, M.P. Tucker, B. Yang, ChemSusChem 10 (2017) 1846–1856;
 (b) J. Liu, Z. Wang, P. Jian, R. Jian, J Colloid Interface Sci. 517 (2018) 144–154.
- [8] (a) F.A. Perras, J.D. Padmos, R.L. Johnson, L.L. Wang, T.J. Schwartz, T. Kobayashi, J.H. Horton, J.A. Dumesic, B.H. Shanks, D.D. Johnson, M. Pruski, J. Am. Chem. Soc. 139 (2017) 2702–2709;
 - (b) M. Zabihi, J. Shayegan, F. Khorasheh, J. Hazard. Mater. 333 (2017) 293-307;
- (c) J. Valand, H. Parekh, H.B. Friedrich, Catal. Commun. 40 (2013) 149–153.[9] (a) N.A.G. -Giordano, A.J. Yeh, A. Okrut, D.J. Xiao, F. Grandjean, G.J. Long,
- S.I. Zones, A. Katz, Chem. Mater. 29 (2017) 6480–6492;
 (b) D. Shen, J. Liu, L. Gan, N. Huang, M. Long, RSC Adv. 7 (2017) 19237–19242.
- [10] (a) C. Parmeggiani, C. Matassini, F. Cardona, Green Chem. 19 (2017) 2030–2050;
 (b) Y. Liu, Y. Zhou, J. Li, Q. Wang, Q. Qin, W. Zhang, H. Asakura, N. Yan, W. Jun, Appl. Catal. B: Environ. 209 (2017) 679–688;
- (c) S. Sharma, S. Sinha, S. Chand, Ind. Eng. Chem. Res. 51 (2012) 8806–8814.
 [11] (a) Z. Jeirani, J. Soltan, Chem. Eng. J. 307 (2017) 756–765;
- (b) M. Shekouhy, A. Moaddeli, A. Khalafi-Nezhad, J. Ind. Eng. Chem. 50 (2017) 41–49;
- (c) R. Hajian, A. Ehsanikhah, Chem. Phys. Lett. 691 (2018) 146-154.
- [12] A.H. Ahmed, Int. J. Chem Tech Res. 6 (2014) 36–52.
- [13] (a) S. Verma, R.B.N. Baig, M.N. Nadagouda, R.S. Varma, ACS Sustainable Chem. Eng. 4 (2016) 2333–2336;
- (b) H. Xia, Z. Liu, Y. Xu, J. Zuo, Z. Qin, Catal. Commun. 86 (2016) 72–76.[14] V.K. Singh, A. Maurya, N. Kesharwani, P. Kachhap, S. Kumari, A.K. Mahato,
- V.K. Mishra, C. Haldar, J. Coord. Chem. 71 (2018) 520-541.
- [15] S. Samanta, R. Srivastava, Appl. Catal. B: Environ. 218 (2017) 621–636.
- [16] E. Gaster, S. Kozuch, D. Pappo, Angew. Chem. Int. Ed. Engl. 56 (2017) 5912–5915.
 [17] E.V. Kudrik, A.B. Sorokin, J. Mol. Catal. A: Chem. 426 (2017) 499–505.
- [17] E.V. Kutin, A.B. Sotokin, J. Mol. Catal. A. Chen. 420 (2017) 495-505.
 [18] Y. Zhanga, T. Yang, B.-Y. Zheng, M.-Y. Liua, N. Xing, Polyhedron 121 (2017) 123-129.
- [19] C. Hu, X. Xia, J. Jin, H. Ju, D. Wu, Z. Qi, S. Hu, R. Long, J. Zhu, L. Song, Y. Xiong, ChemNanoMat 4 (2018) 467–471.
- [20] J. Chai, H. Chong, S. Wang, S. Yang, M. Wu, M. Zhu, RSC Adv. 6 (2016) 111399–111405.
- [21] B. Floris, F. Sabuzi, A. Coletti, V. Conte, Catal. Today 285 (2017) 49–56.
 [22] (a) I. Gryca, K. Czerwińska, B. Machura, A. Chrobok, L.S. Shul'pina,
- M.L. Kuznetsov, D.S. Nesterov, Y.N. Kozlov, A.J.L. Pombeiro, I.A. Varyan,
 G.B. Shul'pin, Inorg. Chem. 57 (2018) 1824–1839;
 (b) P. Sar, A. Ghosh, D. Ghosh, B. Saha, Res. Chem. Intermed. 41 (2015)
- 5565-5586.

- [23] (a) D.C. Crans, L. Yang, A. Haase, X. Yang, Met. Ions Life Sci. 18 (2018) 251–279;
 (b) S. Torabi, M. Mohammadi, M. Shirvani, Trends Pharm. Sci. 4 (2018) 87–94;
 (c) R.P. Pal, V. Mani, D. Tripathi, R. Kumar, N.J. Kewalramani, Biol. Trace Elem. Res. 182 (2018) 248–256.
- [24] (a) Y. Liu, L. Liu, Y. Tan, L. Niu, L. Kong, L. Kang, F. Ran, Electrochim. Acta 262 (2018) 66–73;
- (b) N.S. Chauhan, S. Bathula, A. Vishwakarma, R. Bhardwaj, B. Gahtori, A. Kumar, A. Dhar, ACS Appl. Energy Mater. 1 (2018) 757–764.
- [25] (a) R. Tarasi, A. Ramazani, M. Ghorbanloo, M. Khoobi, H. Aghahosseini, S.W. Joo, A. Shafiee, Silicon 10 (2018) 257–265;
- (b) Y. Ha, M. Mu, Q. Liu, N. Ji, C. Song, D. Ma, Catal. Commun. 103 (2018) 51–55.
 [26] (a) X. Li, B. Lu, J. Sun, X. Wang, J. Zhao, Q. Cai, Catal. Commun. 39 (2013)
 - 115–118;
 - (b) A. Gonzalez-de-Castro, J. Xiao, J. Am. Chem. Soc. 137 (2015) 8206–8218;
 - (c) A. Modak, J. Mondal, A. Bhaumik, Appl. Catal., A 459 (2013) 41–51;
 - (d) A. Bhaumik, R. Kumar, J. Chem. Soc. Chem. Commun. (1995) 349–350;
 (e) P. Basu, T.K. Dey, A. Ghosh, S.M. Islam, J. Inorg. Organomet. Polym. Mater. 28
 (3) (2019) 1158–1170.
- [27] (a) L.T.K. Huyen, N.T. Dat, N.T. Thao, Vietnam J. Chem. 56 (2018) 203–207;
 (b) S.S. Lapari, S. Parham, Int. J. Eng. Sci. Invention 2 (2013) 62–67.
- [28] (a) Z. Sun, G. Li, Y. Zhang, Hai-ou Liu, X. Gao, Catal. Commun. 59 (2015) 92–96;
 (b) Y. Fu, L. Xu, H. Shen, H. Yang, F. Zhang, W. Zhu, M. Fan, Chem. Eng. J. 299 (2016) 135–141.
- [29] G. Zhang, B.L. Scott, R. Wu, L.A. Silks, S.K. Hanson, Inorg. Chem. 51 (2012) 7354–7361.
- [30] (a) H.H. Monfared, R. Bikas, P. Mayer, Inorg. Chim. Acta 363 (2010) 2574–2583;
 (b) P. Saisaha, L. Buettner, M. van der Meer, R. Hage, B.L. Feringa, W.R. Browne, J.W. de Boer, Adv. Synth. Catal. 355 (2013) 2591–2603.
- [31] X. Wang, J. Wu, M. Zhao, Y. Lv, G. Li, C. Hu, J. Phys. Chem. C 113 (2009) 14270–14278.
- [32] A. Aberkouks, A.A. Mekkaoui, B. Boualy, S.E. Houssame, M.A. Ali, L.E. Firdoussi, Adv. Mater. Sci. Eng. (2018), https://doi.org/10.1155/2018/2716435.
- [33] C. Saux, L.B. Pierella, Appl. Catal. A: Gen. 400 (2011) 117–121.
- [34] M.R. Maurya, U. Kumar, P. Manikandan, Dalton Trans. (2006) 3561–3575.
- [35] (a) Y. -ki Yamamoto, A. Miyake, J. Therm. Anal. Calorim. 127 (2017) 743–748;
 (b) J. Petronijević, Z. Bugarčić, G.A. Bogdanović, S. Stefanović, N. Janković, Green Chem. 19 (2017) 707–715;
 (c) B. Pawelec, R.M. Navarro, J.M.C. -Martin, J.L.G. Fierro, Catal. Sci. Technol. 1
- (c) b. Pawerec, N.M. Navario, J.M.C. -Waltin, J.L.G. Pierro, Gatal. Sci. Techniol. 1 (2011) 23–42.
- [36] S.M. Islam, A.S. Roy, P. Mondal, N. Salam, Appl. Organomet. Chem. 26 (2012) 625–634.
- [37] M. Islam, P. Mondal, S. Mondal, S. Mukherjee, A. Singha Roy, M. Mubarak, M. Paul, J. Inorg. Organomet. Polym. 20 (2010) 87–96.
- [38] R. Ando, M. Nagai, T. Yagyu, M. Maeda, Inorg. Chim. Acta 351 (2003) 107–113.
 [39] M. Ramesh, M. Kalidass, M. Jaccob, D. Kaleeswaran, G. Venkatachalam, J.
- Organomet. Chem. 830 (2017) 33-41. [40] S.A. Elsaved, A.M. Noufal, A.M. El-Hendawy, J. Mol. Struct. 1144 (2017) 120-128.
- [41] G.D. Bajju, P. Sharma, A. Kapahi, M. Bhagat, S. Kundan, D. Gupta, J. Inorg. Chem. (2013), https://doi.org/10.1155/2013/982965.
- [42] (a) S.P. Dash, S. Majumder, A. Banerjee, M. Fernanda, N.N. Carvalho, P. Adão, J. Costa Pessoa, K. Brzezinski, E. Garribba, H. Reuter, R. Dinda, Inorg. Chem. 55 (2016) 1165–1182; (2016) 1165–1182;
- (b) H. Zhang, M. Zhou, L. Xiong, Z. He, T. Wang, Y. Xu, K. Huang, Microporous Mesoporous Mater. 255 (2018) 103–109.
- [43] J.D. Benck, Z. Chen, L.Y. Kuritzky, A.J. Forman, T.F. Jaramillo, ACS Catal. 2 (2012) 1916–1923.
- [44] A. Jankeviciute, Z. Károly, N.V. Tarakina, J. Szépvölgyi, A. Kareiva, J. Non-Cryst, Solids 359 (2013) 9–14.
- [45] R.C. Dey, Md.M. Islam, M. Halder, A.S. Roy, S.M. Islam, Chem. Select 1 (2016) 6797–6804.
 [44] G. Cheng, A.S. Asharama, D. Taiarthi, P. Pal, J. Maran, Chem. A 2 (2014).
- [46] S. Ghosh, S.S. Acharyya, D. Tripathi, R. Bal, J. Mater. Chem. A 2 (2014) 15726–15733.
- [47] H.K. Matralis, Ch. Papadopoulou, Ch. Kordulis, A.A. Elguezabal, V.C. Corberan, Appl. Catal. A 126 (1995) 365–380.
- [48] K.T.V. Rao, P.S.N. Rao, P. Nagaraju, P.S. Saiprasad, N. Lingaiah, J. Mol. Catal. A: Chem. 303 (2009) 84–89.
- [49] R.L. Brutchey, I.J. Drake, A.T. Bell, T.D. Tilley, Chem. Commun. (2005) 3736–3738.
 [50] B. Yuan, B. Zhang, Z. Wang, S. Lu, J. Li, Y. Liu, C. Li, Chin. J. Catal. 38 (2017)
- 440-446.
- [51] S. Narayanan, J.J. Vijaya, S. Sivasanker, C. Ragupathi, T.M. Sankaranarayanan, L.J. Kennedy, J. Porous Mater. 23 (2016) 741–752.