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# A chitosan supported peroxidovanadium(V) complex: synthesis, characterization and application as an eco-compatible heterogeneous catalyst for selective sulfoxidation in water

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### Highlights

- ✤ A new polymer immobilized peroxidovanadium(V) complex has been synthesized by reacting V<sub>2</sub>O<sub>5</sub> with 30% H<sub>2</sub>O<sub>2</sub> and the biopolymer chitosan.
- The compound served as a heterogeneous catalyst for the selective oxidation of sulfide with H<sub>2</sub>O<sub>2</sub> in aqueous medium.
- The catalytic protocol provided sulfoxide with an impressive yield and high TOF or TON.
- The catalyst is chemoselective towards the sulfur group in the presence of other oxidation prone functionalities.
- The recyclability of the catalyst for several reaction cycles renders the protocol ecologically sustainable.

### Abstract

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Anchoring of peroxidovanadium(V) (pV) species to chitosan, a natural chelating polymer, afforded a new and structurally defined immobilized complex, VO(O<sub>2</sub>)<sub>2</sub>(NH<sub>2</sub>)-chitosan (**ChpV**) which was comprehensively characterized by elemental analysis (CHN, ICP-OES, energy dispersive X-ray spectroscopy), spectral studies (FT-IR, Raman, <sup>13</sup>C NMR, diffuse reflectance UV-Vis and XPS), SEM, XRD, Brunauer–Emmett–Teller (BET) and thermogravimetric analysis (TGA). Apart from being thermally stable, the compound is water-tolerant and non-hygroscopic. The compound effectively facilitated chemoselective oxidation of thioethers with  $H_2O_2$  in aqueous medium to the respective high purity sulfoxide, in impressive yield (TOF 5628 h<sup>-1</sup>) and with high  $H_2O_2$  efficiency, under mild reaction condition. In addition to water, the heterogeneous catalyst is highly compatible in a variety of organic solvents and is recyclable for several catalytic cycles without significant loss in selectivity. The catalytic procedure is amenable to ready scalability and is free from halogen, co-catalyst and acidic or any other hazardous additive.

Keywords: Peroxidovanadium(V) complex; Chitosan immobilized vanadium(V); Heterogeneous catalysis; Green oxidation catalyst; Aqueous sulfide oxidation.

### 1. Introduction

Currently, with an ever increasing emphasis on the development of cleaner and sustainable chemical processes, efforts towards heterogenization of homogenous catalysts by immobilization of active transition metal complexes on insoluble polymer supports appear to have intensified. Various advantages associated with such systems, including their enhanced stability, specific site selectivity, ease of handling of toxic materials, facile separation and recovery of the catalysts etc., ultimately contributes toward enhancing the overall sustainability of a chemical transformation by minimizing its environmental impact [1].

Apart from cross-linked synthetic organic polymers, natural materials, viz. cellulose, chitin and chitosan, are receiving tremendous contemporary interest as potential polymer supports for immobilization and heterogenization of metal catalysts [1e,2]. Chitosan, the copolymer of 2-amino-2-deoxy-D-glucopyranose and 2-acetamido-2-deoxy-Dglucopyranose, [3] with amino and hydroxyl groups in its structure, exhibits an enormous ability to form metal complexes and has been extensively used in the extraction of metallic impurities from wastewater [4]. Moreover, owing to its attractive physical and mechanical properties, chitosan is also becoming increasingly relevant in a wide variety of applications, including biomedical products [4b,c,5], cosmetics [4b,6], food processing [4b,c,7] etc. Some of the unique features of chitosan and its derivatives which boost their applicability as green supports for heterogenization of metal complexes [2b,3b,4d,8] include: (i) biocompatibility and biodegradability, (ii) non-toxicity, (iii) low cost and eco-friendly, (iv) high metal dispersion on the surface of chitosan, (v) high thermal stability and durability, (vi) physical and chemical versatility, and (vii) insolubility in organic solvents [1e,2b,3b,4d,8]. Several studies have demonstrated chitosan-metal complexes as catalysts in wide range of organic transformations, including C-C bond formation reactions [1e,4d], hydration [1e,4d,9], polymerization [1e], water splitting reactions [9] etc. Nevertheless, reports dealing with the application of chitosan immobilized metal complexes as heterogeneous catalysts in the field of organic oxidation appear to be still scarce [10-12].

It is pertinent to mention here that our group has developed in recent years a series of novel polymer immobilized peroxidometal complexes using  $d^0$  metal ions belonging to group 5 and 6, *viz.* vanadium [13], niobium [14], molybdenum [15] and tungsten [15c, 16], which display excellent activity in a variety of organic oxidations, including phenol hydroxylation [13a], oxidative bromination [13c,15c,16a] and sulfide oxidation [14,15a,16b,16c], under

eco-sustainable reaction conditions. It is however intriguing to note that, despite numerous reports available in the literature on the synthesis and application of peroxidometal complexes as highly efficient and versatile catalysts for organic oxidations [17], we have come across only two reports dealing with the activity of chitosan supported peroxidometal derivatives as oxidation catalysts [18]. For example, Zhu *et al.* reported a chitosan supported protonated peroxidotungstate (**pW**) system which efficiently catalysed the oxidation of a variety of organic substrates in acetonitrile [18a].

In the present work we have explored the scope of generating a new heterogeneous oxidation catalyst, by immobilizing peroxidovanadate (pV) species on chitosan. Vanadium has been considered an adequate choice for our study, as vanadium based catalysts are known to support environmentally benign aerobic oxidation conducted in water [17a,19]. Furthermore, vanadium, with its well-established biological and therapeutic roles, exhibits diverse chemistry owing to its easily accessible oxidation states and rich coordination chemistry, which have led to its application in various fields including catalysis, both homogeneous and heterogeneous [12b,17a,19,20].

Among the great variety of organic oxidations, one of the industrially as well as fundamentally most important transformations is known to be the chemoselective oxidation of organic sulfides. Sulfoxides and sulfones serve as versatile synthetic intermediates for the construction of chemically and biologically significant molecules, including chiral auxiliaries and therapeutic agents [21]. Since the earliest synthesis of sulfoxides via the oxidation of sulfides by Maercker in 1865 [22], numerous oxidation strategies have been introduced for the successful synthesis of sulfoxides or sulfones using a vast range of traditional oxidants [22a,23]. The identification of aqueous  $H_2O_2$  as the ideal non-polluting and green oxidizing agent [20e,21e,24] for the oxidation of sulfides spurred the development of a plethora of useful and promising transition metal catalysts over the vears [12a,b,c,14,15a,b,20,21f,g,24b,25-29] to facilitate H<sub>2</sub>O<sub>2</sub> induced sulfide oxidation. However, many of these methodologies utilized hazardous and toxic reagents and solvents or complex procedures often resulting in unwanted by-products [30]. So, the ever increasing demand for newer alternative catalysts and sustainable oxidation procedures that can operate under environmentally benign reaction conditions, implementing safer reagents and non-polluting reaction media, continues.

Owing to the recognition of water as a natural green solvent [31] which can often be used as an alternative to traditional organic solvents [31a-d,32], an upsurge in contemporary interest in water-centred organic synthesis has been witnessed recently [32]. Due to its

abundance, low cost and inherent properties, such as polarity, viscosity, high heat capacity, environment compatibility, non-toxicity and non-flammability, [31a,32] water can be a great asset to the reaction. Along with the increasing importance of water-based organic reactions, the need for the development of water-tolerant and water compatible catalysts to support such transformations is rising tremendously. It is notable that whereas the majority of the available studies on metal catalysed sulfide oxidations conducted in aqueous medium focused on developing water soluble catalysts [14,15a,20a,b,25a,f,28], reports pertaining to still heterogeneously catalysed thioether oxidation in water are very limited. [24b,27b,c,d,31f]

Herein, we discuss the preparation and characterization of a new chitosan anchored pV complex, as well as its performance as a heterogeneous catalyst for the controlled oxidation of sulfide to sulfoxide in aqueous medium, in terms of selectivity, reusability, TOF, scalability and sustainability. To the best of our knowledge, this is the first example related to the preparation and use of a well-defined peroxidovanadate compound supported on chitosan as a catalyst for organic oxidation.

### 2. Experimental

### 2.1 Materials

Acetone, methanol, ethylacetate, ethanol, hydrogen peroxide, petroleum ether (RANKEM), diethyl ether, sodium hydroxide (E. Merck, India), silica gel (60-120 mesh), vanadium pentoxide (Sisco Research Laboratories), chitosan (medium molecular mass, deacetylated degree 85%, viscosity 200-800 cps), methyl phenyl sulfide (MPS), methyl p-tolyl sulfide (MpTS), ethyl phenyl sulfide (EPS), dimethyl sulfide (DMS), dibutylsulfide (DBS), 2-(phenylthio)ethanol (PTE), dihexylsulfide (DHS), diphenylsulfide (DPS) and allyl phenyl sulfide (APS) were obtained from Sigma–Aldrich Chemical Company, Milwaukee, USA. The water used for solution preparation was deionized and distilled.

# 2.2 Synthesis of the chitosan anchored peroxidovanadium complex $VO(O_2)_2(NH_2)$ -chitosan (ChpV)

The procedure adopted for the synthesis of **ChpV** is as follows:  $V_2O_5$  (0.56 g, 3.08 mmol) was dissolved in 30% H<sub>2</sub>O<sub>2</sub> (10 mL, 89.28 mmol) maintaining the temperature below 4 °C. The initial pH of the resulting clear yellow solution was found to be *ca.* 1. Concentrated

potassium hydroxide (*ca.* 8 M) was then added dropwise to raise the pH of the solution up to *ca.* 7 with constant stirring. Keeping the reaction mixture stirred in an ice-bath, 1 g of chitosan was added to it. The resulting reaction mixture was allowed to stand for 24 h under constant stirring, maintaining the temperature below 4 °C. Subsequently, the supernatant liquid was decanted and the resulting yellowish residue was washed repeatedly with acetone. The product was then dried in *vacuo* over concentrated sulfuric acid and kept in refrigerator. The catalyst was found to be non-hygroscopic and stable for several weeks.

Found: C, 28.78; H, 5.55; N, 6.32; K, 9.67; V, 11.90;  $O_2^{2^-}$ , 14.98%. The metal loading calculated from the observed vanadium content is 2.34 mmol g<sup>-1</sup> of polymer for  $VO(O_2)_2(NH_2)$ -chitosan (**ChpV**).

#### 2.3 Elemental analysis

The vanadium content of the synthesized compound was determined by atomic absorption spectroscopy (AAS) employing a Thermo iCE 3000 series atomic absorption spectrophotometer (model analyst 200) and an inductively coupled plasma optical emission spectrophotometer (ICP-OES) (Perkin Elmer, OPTIMA 2100 DV), along with volumetrically by the iodometric method described in an earlier paper [33]. The potassium content was also measured by ICP-OES. Elemental analysis for C, H and N was carried out on an elemental analyzer (Perkin-Elmer 2400 series II). The peroxide content of the compound was determined by the procedure reported previously [14,15a,b].

### 2.4 Physical and spectroscopic measurements

The IR spectra were recorded by making pressed pellets of samples with KBr disks using a Perkin-Elmer spectrum 100 FTIR spectrophotometer. The raman spectrum of the compound was recorded using a Renishaw InVia Raman microscope equipped with an argon ion laser with an excitation wavelength of 514 nm and a laser maximum output power of 20 mW. The diffuse reflectance electron absorption spectra were measured using a Hitachi U-3400 spectrophotometer equipped with a diffuse reflectance accessory with an integrating sphere of 60 mm inner diameter and using BaSO<sub>4</sub> as the standard. The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer (Miniflax, UK) using Cu Ka ( $\lambda = 0.154$  nm) radiation at a scanning rate of 10 °C min<sup>-1</sup> in the 20 range 10–70°. XPS measurements were carried out by using a Thermo Fisher Scientific Instrument's X-ray photo spectrometer equipped with an Al Ka (monochromatic) X-ray source. The source was

operated at 12 kV. The base pressure was maintained at 2 x 10<sup>-9</sup> mbar in the analysing chamber. Charging of the samples was corrected by setting the binding energy of the adventitious carbon (C 1s) at 284.6 eV. Thermogravimetric analysis (TGA) was carried out on a SHIMADZU TGA-50 system at a heating rate of 10 °C min<sup>-1</sup> under a N<sub>2</sub> atmosphere using an aluminium pan. Scanning electron microscopy (SEM) and Energy-dispersive X-ray analysis of the compound were obtained using a JEOL JSM-6390LV scanning electron micrograph attached with an energy-dispersive X-ray detector. Scanning was done in the 1-20 µM range, and images were taken at a magnification of 15–20 kV. Data were obtained using INCA software. Standardization of the data analysis is an integral part of the SEM-EDX instrument employed. The <sup>13</sup>C NMR spectra for chitosan and ChpV were recorded using a JEOL JNM-ECX400II spectrometer at a carbon frequency of 100.5 MHz, 1024 Xresolution points, number of scans 1300, 29 ms of acquisition time and 5 s of relaxation delay. <sup>51</sup>V NMR spectra were recorded on a JEOL JNM-ECS400 spectrometer at a vanadium frequency of 105.154 MHz with the samples in a 10 mm spinning tube using a sealed coaxial tube containing D<sub>2</sub>O, which provided the lock signal. The chemical shift data were recorded as negative values of ppm ( $\delta$ ) in the low-frequency direction with reference to VOCl<sub>3</sub> at 293 K. The surface areas were determined by nitrogen adsorption/desorption measurements based on the Brunauer-Emmett-Teller (BET) method at 77.3 K on a standard module NOVA 1000E, Quantachrome Instrument. The pore size and pore volumes were measured by the Barrett-Joyner-Halenda (BJH) model in the same Quantachrome Instrument. Magnetic susceptibilities of the complex were measured by the Gouy method, using Hg[Co(NCS)] as the calibrant. The melting points of the products were determined in open capillary tubes on a Büchi Melting Point B-540. The GC analysis was done using a CIC model 2010 gas chromatograph and an SE-52 packed column (length 2 m, 1/8 inch OD) with a flame ionization detector (FID) and nitrogen as the carrier gas (30 mL min<sup>-1</sup>).

### 2.5 General procedure for the catalytic oxidation of sulfides to sulfoxides

In a representative procedure, the organic substrate MPS (5 mmol) was added to the reaction mixture consisting of the catalyst (21.00 mg, containing 0.005 mmol of V) in 5 mL of H<sub>2</sub>O. Then 30% H<sub>2</sub>O<sub>2</sub> (2.82 mL, 25 mmol) was added to the reaction system, contained in a round bottom flask. The molar ratio of V:substrate and that of substrate:H<sub>2</sub>O<sub>2</sub> was maintained at 1:1000 and 1:5, respectively. For the reaction conducted in acetonitrile, the V:substrate and the substrate:H<sub>2</sub>O<sub>2</sub> ratios were adjusted to 1:1000 and 1:2, keeping the other reaction conducted at

ambient temperature under continuous magnetic stirring. The progress of the reaction was monitored by thin layer chromatography (TLC) and GC. After completion of the reaction, the catalyst was separated by filtration and washed with acetone. The product and the unreacted substrates were extracted with diethyl ether from the filtrate, dried over anhydrous sodium sulphate and distilled under reduced pressure to remove excess solvent. The obtained product was purified by column chromatography on silica gel using ethyl acetate-hexane (1:9) as the eluent. The product was characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and melting point determination for solid products [Text S1 (Supplementary Information)].

### 2.6 Regeneration of the catalyst

The recyclability of the catalyst was tested using MPS as a model substrate. After completion of the reaction, the catalyst was separated by centrifugation, washed with acetone and dried in *vacuo* over concentrated sulfuric acid. Diethyl ether was used to extract the unreacted substrate and product. To repeat the experiment, the recovered catalyst was added to a fresh batch of MPS (0.59 mL, 5 mmol) and 30%  $H_2O_2$  (2.82 mL, 25 mmol in water or 1.13 mL, 10 mmol in acetonitrile) in 5 mL solvent (water or acetonitrile). The reaction was allowed to proceed under the optimized conditions. The reusability of the catalyst was tested up to 5 reaction cycles independently in both CH<sub>3</sub>CN and H<sub>2</sub>O. The recycled catalyst was characterized by IR spectroscopy and ICP-OES.

### 3. Result and Discussion

### 3.1 Synthesis and characterization

In the present study, the synthetic strategy developed for obtaining the desired immobilized catalyst, **ChpV**, was based on the reaction of *in-situ* generated pV species with chitosan under fairly mild reaction conditions (Scheme 1). The reaction was carried out in water at neutral pH and at ice-bath temperature. As chitosan is known to be water soluble under acidic conditions [34], the pH of the reaction medium was stringently maintained above *ca*.7 in order to obtain the solid catalyst in a water insoluble form. The alkali used to adjust the pH of the reaction solution also served as the source of the counter cation for the pV complex anions formed. It is notable that in contrast to the highly hygroscopic nature usually observed for monomeric peroxidovanadium complexes [13c,35], the supported catalyst **ChpV** has been observed to be non-hygroscopic and stable for weeks, without any change in its catalytic activity.

#### <Scheme 1>

The newly synthesized catalyst has been characterized by elemental analysis, TG-DTG analysis and a combination of spectroscopic techniques, such as IR, Raman and electronic spectral studies, SEM-EDX, ICP-OES, powder XRD, XPS, BET analysis and <sup>13</sup>C NMR study etc. The presence of two peroxido groups per vanadium centre in the compound was confirmed from elemental analysis data, showing the  $V:O_2^{2^-}$  ratio as 1:2. The elemental analysis data complemented by inductively coupled plasma-optical emission spectrophotometer (ICP-OES) analysis and EDX spectral analysis results showed the vanadium loading on chitosan to be 2.34 mmol metal per gram of the polymeric support. The occurrence of vanadium in the compound in its +5 oxidation state was confirmed by magnetic susceptibility measurement, which showed the diamagnetic nature of the complex **ChpV**.

### 3.1.1 SEM and energy dispersive X-ray (EDX) analysis

The scanning electron micrograph of the compound **ChpV** showed considerable roughening of the surface compared to the free polymer chitosan, as seen in Figs. 1(a) and (b). This morphological change of the surface of the compound is due to the adsorption or dispersion of the peroxidometallates on the pristine polymer surface.

#### <Fig. 1>

The presence of K and V along with C, O and N in the supported pV catalyst has been confirmed further from the energy dispersive X-ray analysis results [Fig. 1(c)]. EDX analysis has been carried out by focusing on multiple regions over the surface of the catalyst. The composition of the compound as obtained by EDX analysis is in close agreement with the elemental analysis data.

### **3.1.2 X-ray diffraction studies**

The X-ray diffraction patterns of chitosan and the metal incorporated polymer immobilized catalyst, **ChpV**, are presented in Fig. 2. The X-ray diffractogram of chitosan displayed three main diffraction peaks at 2 $\Theta$  values of *ca.* 12.7, 19.97 and 26.7°, which correspond to the semi-crystalline nature of the polymer [36]. In the diffractogram of **ChpV**, the intensities of the characteristic peaks of chitosan were observed to weaken with the concomitant appearance of many new diffraction peaks, indicative of the formation of a new crystalline

phase [4a,e,37]. The decrease in intensity of the peaks corresponding to chitosan is likely to be due to the disruption of hydrogen bonds within chitosan owing to incorporation of the metal complex [4e,37,38]. This may be a plausible factor responsible for the relatively lower thermal stability of the catalyst, as has been demonstrated by TGA results. The additional sharp diffraction peaks in the diffractogram of the **ChpV** complex, were located at 2 $\Theta$  values of 14.4, 15.3, 17.7, 25.2 and 28.6°. These values are close to the ones observed for peroxidovanadium species (PDF 81-2392) and may be ascribed to the (001), (200), (<u>2</u>01), (110) and (<u>2</u>02) planes, respectively. These observations confirmed the anchoring of the peroxidovanadium moiety to the polymer matrix.

<Fig. 2>

#### 3.1.3 X-ray photoelectron spectroscopy

The XPS spectrum of **ChpV** is presented in Fig. 3. This technique is important for analyzing the electronic properties of the species on the surface. The complex displayed characteristic peaks for vanadium  $(2p_{3/2} \text{ and } 2p_{1/2})$  at 517.5 and 525.0 eV, respectively, with a splitting difference of *ca*. 7.5 eV, which is close to the value reported for V<sub>2</sub>O<sub>5</sub> [39]. The binding energy values suggest the presence of vanadium in the + 5 oxidation state in the complex on the basis of the available literature [39,40]. The O 1s peak is observed at 533.0 eV with a shoulder at 530.9 eV. This may be due to oxygen from both the chitosan support and the metal peroxido system, respectively [39d,41]. Thus, the XPS study confirms the immobilization of the pV complex on chitosan.

<Fig. 3>

### 3.1.4 BET analysis

The surface areas of the polymer, chitosan and metal incorporated complex **ChpV** were measured using BET analysis with the nitrogen adsorption method and the pore volume was determined by the BJH model [42]. The N<sub>2</sub> adsorption/desorption isotherm of the compound showed a typical type II adsorption (Fig. 4) of an IUPAC standard for particles which have macropores or non-pores showing poor adsorption [43]. The average specific surface area of the vanadium incorporated metal complex **ChpV** was found to be 43.6 m<sup>2</sup>/g, which is considerably greater than that of the pristine polymer (3.0 m<sup>2</sup>/g) (Table 1). Thus, it is evident that complexation of chitosan with vanadium results in affirmative changes in the surface

morphology of the polymer. The value of the constant C in the BET equation was in the range (2-200), which is characteristic of multilayer adsorption (type II isotherm) [44].

<Table 1>

<Fig. 4>

#### 3.1.5 IR and Raman spectral studies

Significant features of the IR spectra of chitosan and ChpV are summarized in Table S1 [Supplementary Information]. Characteristic differences were observed between the spectral patterns originating from the vanadium anchored chitosan and free chitosan. As seen in Fig. 5, the IR spectrum of the initial free chitosan exhibits typical peaks located at approximately 3434 (O-H stretch and N-H stretch), 2921 (-CH<sub>3</sub> stretch), 2876 (-CH<sub>2</sub> stretch), 1592 (N-H bending), 1154 (bridge O stretch) [38a,45] and 1646 cm<sup>-1</sup>(C–O stretching along with N–H deformation mode, amide I) [4e,46]. In the spectrum of the compound ChpV, there is no distinct shift observed in the position of the amide I band of the complex compared to the untreated polymer, indicating that the amide group is not involved in coordination with the metal. The possibility of coordination through the N atom of the amide group is also not likely as such coordination causes a considerable decrease in the carbonyl stretching frequency, which is not the case for the ChpV complex [16a,47]. The peak at 3434 cm<sup>-1</sup>, corresponding to the stretching vibrations of the -NH<sub>2</sub> and -OH groups, showed a considerable shift to a lower frequency of 3199 cm<sup>-1</sup>, suggesting that either the -NH<sub>2</sub> or -OHgroup takes part in complexation [4a,b,37a,38a,45,48]. However, the peak attributed to the bending vibration of the -OH group and the band assigned to the secondary -OH group at 1421 and 1089 cm<sup>-1</sup>, respectively remained unaltered in the spectrum of the complex, negating the possibility of the -OH group taking part in chelation [4a,b,34b,37a,48,49]. However, the –NH bending vibration of the free amine group in chitosan is shifted to a lower wavenumber in the complex, ChpV. It was observed that both the stretching and bending vibrations of the -NH<sub>2</sub> group shifted to a lower value in the complex, because coordination of chitosan through the nitrogen centre with the metal ion would possibly reduce the electron density of the amino group [4a,b,e,12a,37a,38a,46a,48]. This confirmed the coordination of the vanadium(V) center with chitosan through the  $-NH_2$  group [4a,b,e,37a,38a]. The band at 642 cm<sup>-1</sup>, ascribed to V-N bond, further signifies the complexation of the metal with chitosan [4b,8b,37,38,50] through the  $-NH_2$  group. Moreover, the band at 1038 cm<sup>-1</sup> of chitosan remain unaffected in ChpV, which means that the primary -OH group is not involved in

complexation [4e,48]. The characteristic bands of chitosan, the  $\beta$ -(1–4) glycoside bridge bands (at around 1,154 and 894 cm<sup>-1</sup>), were also seen in the FT-IR spectra of **ChpV**, indicating that the metal complex successfully anchored to chitosan without altering the main backbone of chitosan [4e,38b,46c,50a].

Apart from the typical bands due to the chitosan support, the IR spectrum of **ChpV** enabled the clear identification of diagnostic peaks attributable to the terminal oxido and peroxido groups of the  $[VO(O_2)_2]$  moiety, with an intense band at 939 cm<sup>-1</sup> and absorptions at *ca*. 869, *ca*. 616 and *ca*. 525 cm<sup>-1</sup> representing the v(V=O), v(O-O), v<sub>asym</sub>(V-O<sub>2</sub>) and v<sub>sym</sub>(V-O<sub>2</sub>) modes, respectively [13b,51]. The Raman spectrum of the catalyst complemented the IR results, displaying well-resolved bands corresponding to v(O-O), v<sub>asym</sub>(V-O<sub>2</sub>), v<sub>sym</sub>(V-O<sub>2</sub>) and v(V=O) in the vicinity of *ca*. 895, *ca*. 628, *ca*. 542 and *ca*. 956 cm<sup>-1</sup>, respectively (Fig. 6).

<Fig. 5>

<Fig. 6>

### 3.1.6 Electronic spectral studies

The diffuse reflectance UV-visible spectrum of the compound **ChpV** showed two bands at around 350 and 245 nm (Fig. 7). The band appearing at 350 nm is assigned to a peroxido to metal transition (LMCT), which is characteristic of a diperoxido species of vanadium(V) [13b,c]. The band at 245 nm in the spectrum of **ChpV** is assigned to the typical  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions of the chitosan support [38a,48,52].

<Fig. 7>

### 3.1.7<sup>13</sup>C and <sup>51</sup>V NMR studies

The <sup>13</sup>C NMR spectrum of the catalyst along with the spectrum of free chitosan recorded in the solid state are presented in Fig. 8. The corresponding resonances are listed in Table 2 for comparison. The assignments are on the basis of available literature data [3a,53], however, the exact resonance position may vary slightly according to the NMR technique used (solid or liquid state analysis). The <sup>13</sup>C NMR spectrum of chitosan displays characteristic resonances at  $\delta$  58.7, 62.3, 85.1 and 106.3 ppm attributable to the C-2, C-6, C-4, and C-1 carbon atoms, respectively. The resonance centered at  $\delta$  76 ppm probably originates from a combination of the C-3 and C-5 signals, as has been reported [53d]. As the chitosan used was highly deacetylated, no observable peaks at around  $\delta$  174 and 24 ppm, characteristic of the carbon

atoms of the –C=O and –CH<sub>3</sub> groups, were found in the spectrum, as anticipated [53a,b]. The comparison of the NMR spectra before and after loading of the pV moiety showed distinct changes in the spectrum of the catalyst, (as seen in Table 2) although the overall spectral pattern of the catalyst **ChpV** resembled closely the spectrum of free chitosan by exhibiting major peaks at  $\delta$  57.7, 62.7, 85.8 and 100.5 ppm due to the C-2, C-6, C-4, and C-1 carbon atoms. However, the spectrum showed a distinct shift of the resonance positions of the carbon atoms of chitosan along with a broadening of the signals in comparison to the original chitosan spectrum, indicating a change in environment of the C atoms after metal anchoring [53b,c]. The intensity of the signal corresponding to the C-2 atom attached to the –NH<sub>2</sub> group was shifted by nearly 1 ppm and appeared as a weaker intensity shoulder along with the peak at  $\delta$  62.7 ppm in the spectrum of the catalyst. Moreover, the C-1 signal showed a considerable shift and the spectrum of the catalyst enabled clear identification of the C-3 and C-5 signals at  $\delta$  100.5 and 76.8 ppm, respectively. It is significant to note that no new resonance was seen in the spectrum at around  $\delta$  175 ppm, attributable to the –COOH group. Thus, from the NMR analysis it has been confirmed that although the chitosan structure undergoes modification owing to anchoring of the pV species, the main backbone structure of chitosan does not change during complexation with V(V) [54].

### <Fig. 8>

### <Table 2>

The <sup>51</sup>V NMR spectral analysis of the compound **ChpV** furnished further evidence to suggest anchoring of perxidovanadium moieties to the chitosan polymer. The spectrum of the compound shown in Fig. 9, displayed a resonance at  $\delta$  -690 ppm, which is in the region typical of a diperoxidovanadate species. The peak has been assigned on the basis of available literature [13c,15b,35b].

#### <Fig. 9>

#### **3.1.8** Thermal analysis

The thermal degradation behaviour of chitosan, as well as chitosan-metal complexes, has been extensively investigated in recent years [4b,e,11,12a,37b,38b,c,55]. Apart from the initial water loss stage below 100 °C, chitosan exhibits a single stage decomposition in the range 270-315 °C, with a mass loss of 33.1% due to the degradation of the polymer, including deacetylation. The polymer undergoes further degradation up to 700 °C. In the majority of

the reports, it has been observed that complexation of chitosan with metals usually lowers the thermal stability of the polymer [4b,e,11,12a,37b,38b,c,55].

The TG-DTG profile of the chitosan anchored pV compound showed a multistage degradation upon heating up to 700 °C (Fig. 10, Table 3). After the first decomposition step due to dehydration occurring in the temperature range below 100 °C, the subsequent degradation occurred in the temperature range 139-182 °C with a mass loss of 12.7%. This step has been ascribed to the loss of peroxido groups from the chitosan anchored pV species. Thereafter, on increasing the temperature, the compound undergoes further degradation in the range 226-310 °C due to the cleavage of the glycosodic linkage in the chitosan backbone [4e,38c] with a mass loss of 21.6%. Thus the step corresponding to degradation of the chitosan support occurs at a lower temperature in the catalyst ChpV, compared to free chitosan, indicating a relatively lower thermal stability of the pV-chitosan complex, in agreement with the previous finding [4b,e,11,12a,37b,38b,c,55]. The black residue remaining after complete degradation of the catalyst ChpV was found to be 59.8%. The FTIR spectrum of the residue displayed the typical v(V=O) bands of oxidovanadium species. The chitosan bands of the original compound nearly disappeared in the spectrum of the residue, which is in accord with a previous report showing that the characteristic bands of chitosan disappear in the char residue obtained after thermal degradation of chitosan on heating up to a temperature of 600 °C [56]. Thus, it has been confirmed that the residue from the chitosan immobilized pV complex ChpV consists of an oxidovanadium compound along with the char residue of the polymer.

### <Fig. 10>

#### <Table 3>

Based on the above collective evidences, a structure of the type shown schematically in Fig. 11 has been envisaged for the macromolecular complex **ChpV**. It is worthy to mention that different models have been proposed previously [4a,b,f] to describe the mode of metal ion-chitosan coordination, such as the 'bridge model' and 'pendant model'. In the bridge model, the metal ion is usually bound with four nitrogen atoms from the same chain or from different chains, whereas in the pendant model, the metallic ion is linked to the amino group as a pendant. In case of the catalyst **ChpV**, the structure shows the coordination of the V(V) centre of the pV moiety to the amino group of chitosan to form a 'pendant complex'.

<Fig. 11>

#### 3.2 Catalytic activity of the supported complex ChpV

#### 3.2.1 Oxidation of sufides to sulfoxides

We have explored the catalytic performance of the chitosan immobilized pV compound, **ChpV**, as a heterogeneous catalyst in the selective oxidation of organic sulfides to sulfoxides using 30% H<sub>2</sub>O<sub>2</sub> as a terminal oxidant, under a variety of reaction conditions. In order to optimize the reaction conditions to achieve the best conversion and selectivity, the influence of key factors, such as type of solvent, substrate:H<sub>2</sub>O<sub>2</sub> stoichiometry, catalyst concentration etc., were investigated using methyl phenyl sulfide as a representative substrate. Details of the study are shown in Table 4.

#### **3.2.1.1 Effect of concentration of the oxidant**

In an exploratory experiment, the reaction of MPS with  $H_2O_2$ , maintaining an MPS: $H_2O_2$ molar ratio of 1:2 and a catalyst:substrate ratio of 1:1000, was conducted in aqueous medium at ambient temperature under magnetic stirring. As evident from the data presented in Table 4 (entry 1), under these conditions MPS was completely transformed into the sulfoxide with 100% selectivity. The TOF could be improved further by increasing the amount of oxidant gradually from 2 to 5 equivalents. More than a 10-fold rise in the TOF (Table 4, entry 4) could be achieved with 5 equivalents of  $H_2O_2$ , without affecting the selectivity of the reaction. Interestingly, a further increase in the oxidant amount to 6 equivalents led to over oxidation of sulfoxide to sulfone, rendering the reaction non-selective, although a substantial increase in TOF occurred (Table 4, entry 5).

#### <Table 4>

#### 3.2.1.2 Effect of catalyst amount

Apart from the oxidant concentration, the amount of catalyst was observed to have a significant influence on the rate and selectivity of the sulfide oxidation. As illustrated in Table 4 (entry 6), the catalyst was found to be effective even at a V:substrate molar ratio of 1:2000, affording a reasonably good TOF. An increase in the catalyst amount (Table 4, entry 7) accelerated the process as expected, however, the reaction resulted in a reduced TOF and

partial over oxidation of sulfoxide to sulfone. Thus, for achieving a high conversion without compromising the sulfoxide selectivity in aqueous medium, a catalyst:substrate molar ratio of 1:1000 and a substrate:oxidant ratio of 1:5 have emerged to be optimal.

The importance and role of the catalyst in facilitating the formation of the target product was confirmed by conducting a control experiment in the absence of the catalyst. The reaction under such conditions was found to be rather slow and non-selective, leading to the formation of both sulfoxide and sulfone in < 12% yield (Table 4, entries 16 and 17) within the stipulated reaction time. With the aim of comparing the activity of the heterogeneous pV catalyst with the homogeneous one, we have conducted the oxidation reaction using a diperoxidovanadate previously reported water soluble monomeric complex,  $K[VO(O_2)_2(H_2O)]$  (DPV) [57], in lieu of the heterogeneous pV catalyst, ChpV, maintaining a similar catalyst concentration (V:MPS of 1:1000). As can be seen from the results in Table 4 (entries 18,19), in the presence of the free complex species,  $[VO(O_2)_2(H_2O)]^2$ , the TOF obtained was nearly half of that afforded by the polymer supported heterogeneous catalyst ChpV under otherwise analogous reaction conditions. Moreover, the DPV catalysed reaction provided a mixture of sulfoxide and sulfone and hence was found to be less selective.

#### **3.2.1.3 Effect of solvent**

We have also screened the performance of the catalyst in common organic solvents, in addition to water. In order to assess the solvent effect, we have chosen relatively safer organic solvents such as methanol, ethanol and acetonitrile for the oxidation of MPS [58]. It is pertinent to mention that in the present study, we have strategically avoided the use of hazardous chlorinated solvents. To our pleasure, as seen from the data depicted in Table 4, the catalytic protocol for sulfoxidation was observed to be compatible with each of the tested organic solvents. In fact, the catalyst turned out to be more potent in organic solvents compared to water, providing the best results in acetonitrile with respect to both product selectivity and TOF, even with 1 equivalent of  $H_2O_2$  (Table 4, entry 8). This may not be surprising in view of the complete solubility of the organic substrate in these solvents. Nearly a 4-fold improvement in the TOF could be achieved in acetonitrile simply by increasing the amount of oxidant to 2 equivalents and maintaining the catalyst:substrate ratio as 1:1000 (Table 4, entry 9). A further increase in amount of oxidant, however, led to a loss of selectivity of the reaction (Table 4, entry 10). Thus, in acetonitrile a substrate:oxidant molar ratio of 1:2 was found to be optimal (Table 4, entry 9). Moreover, as can be seen from the

results presented in Table 4 (entry 9), a catalyst:substrate ratio of 1:1000 also proved to be conducive to attain the best conversion in acetonitrile. It is thus remarkable that the same catalyst enabled us to achieve selective oxidation of sulfides in aqueous medium as well as in organic solvents by versatile variation of the reaction conditions, as shown in Table 4.

Subsequently, we have extended the study to a range of structurally diverse sulphides, such as dialkyl, diaryl, aryl alkyl, aryl allyl, aryl alcohol etc., in experiments conducted independently in water as well as acetonitrile under the respective standardized reaction conditions. The results, depicted in Tables 5 and 6, demonstrate that excellent yields with complete selectivity were possible to be attained with the series of substrates examined in the presence of the catalyst. Importantly, no over oxidation of sulfoxide to sulfone was observed in any of the tested substrates under the investigated conditions.

That the nature of the substituent influenced the rate of oxidation was evident from the variations in the TOF values within the substrates examined. Dialkyl sulfides were oxidized by  $H_2O_2$  at a faster rate with a higher TOF compared to allylic sulfides. In fact, dimethyl sulfide was oxidized with the highest TOF of 5628 and 5688 h<sup>-1</sup> in water and acetonitrile, respectively (Table 5, entry 2 and Table 6, entry 2). On the other hand, in case of a conjugated system, such as diphenylsulfide, the reaction was found to be rather sluggish with a relatively poor TOF (Table 5, entry 9 and Table 6, entry 9). The observed trend in the rates of oxidation is in accord with the decreasing nucleophilicity of the thioethers examined. As it is known that sulfide oxidation by  $H_2O_2$  generally occurs *via* an electrophilic addition reaction of an oxygen atom to the substrate [59], it is expected that thioethers such as alkyl sulfides with a higher electron density on the sulfur atoms would react faster compared to conjugated systems, such as aromatic and allylic sulfides.

### <Table 5>

#### <Table 6>

An additional attractive feature of the methodology, irrespective of the solvent used, is the excellent chemoselectivity of the catalyst towards the sulfur group of the substituted sulfides with other oxidation prone functional groups. Thus, allylic and alcoholic sulfoxides were obtained without affecting any other functional group transformation (Table 5, entries 7,8 and Table 6, entries 7,8). The protocol for sulfide oxidation was also applied for the high scale synthesis of sulfoxide up to ten-fold under optimized conditions (Table 5, entry 1<sup>c</sup> and

Table 6, entry 1<sup>c</sup>). The H<sub>2</sub>O<sub>2</sub> efficiency in the oxidation reaction under the optimized conditions was found to be greater than 90% for all substrates, except for diphenyl sulfide (67% in H<sub>2</sub>O and 73% in CH<sub>3</sub>CN), complementing the higher activity of the catalyst within a reasonably short reaction time in both CH<sub>3</sub>CN and H<sub>2</sub>O. The efficiency was measured as 100  $\times$  moles of H<sub>2</sub>O<sub>2</sub> consumed in the formation of the oxyfunctionalized products per mole of H<sub>2</sub>O<sub>2</sub> converted [Text S2 (Supplementary Information)] [60].

#### 3.2.2 Test for the heterogeneity of the reaction

To confirm the heterogeneity of the reaction, separate experiments were carried out using MPS as te substrate under standard protocols. After completion of the reaction, the solid catalyst was separated by filtration and the filtrate was treated with a fresh batch of MPS and 30% H<sub>2</sub>O<sub>2</sub>. The reaction was allowed to continue for another 1h. It was found that the conversion was very low, only about 11% in H<sub>2</sub>O (9% in CH<sub>3</sub>CN), which is close to the conversion obtained from the control experiment conducted in the absence of a catalyst (Table 4, entries 16,17). That the reaction did not proceed on removal of the catalyst was thus evident. Moreover, the absence of vanadium in the filtrate obtained after separating the solid catalyst was ascertained by ICP-OES analysis. These observations refute the possibility of leaching of the metal complex from the polymer incorporated catalyst into the reaction medium during the oxidation reaction, which further proves the heterogeneity of the catalytic process.

### 3.2.3 Recyclability of the catalyst

Owing to the heterogeneous nature of the catalyst, it could be easily separated from the spent reaction mixture and recharged in the subsequent reaction run. The recyclability of the catalyst was tested for five reaction cycles using MPS as the substrate. Recycling experiments were performed by charging the spent catalyst with a fresh batch of substrate,  $H_2O_2$  and the respective solvent (CH<sub>3</sub>CN or H<sub>2</sub>O) after completion of each reaction cycle. The catalyst could be reused for at least up to five reaction cycles with consistent activity and selectivity when acetonitrile was used as the solvent (Table 6 and Fig. 12). The FT-IR spectrum of the spent catalyst showed the characteristic bands corresponding to chitosan and the metal-peroxido stretching, as has been observed in the spectrum of the original catalyst (Fig. 13). Moreover, no significant decrease in the vanadium content value of the recovered catalyst was indicated by the ICP-OES analysis and EDX spectral data compared to the starting catalyst. In the case of the reaction conducted in water, the catalyst could be reused with

consistent activity and selectivity up to the 3<sup>rd</sup> cycle, after which a slight decrease in activity was noted, indicating a small amount of leaching of the pV species (Table 5 and Fig. 12).

<Fig. 12>

<Fig. 13>

#### 3.2.4 Proposed catalytic cycle

In order to explain our observations pertaining to the catalytic activity displayed by the chitosan immobilized catalyst in the sulfoxidation reaction, a plausible catalytic cycle, as shown in Fig.14, is proposed. Our previous findings on the oxidant activity of pV complexes, as well as ample evidences available in the literature, have shown that vanadium(V) peroxido complexes act as electrophilic oxygen transfer agents, reacting preferentially with the most nucleophilic group of the substrate molecule [13b,c,17a-d,58c,d,61]. It is therefore expected that the first step in the proposed scheme of reaction would be the facile transfer of the electrophilic oxygen atom from the diperoxido vanadium species (I) to the sulphide, yielding sulfoxide as the product, with the concomitant transformation of the catalyst into a dioxidemonoperoxidovanadium intermediate II (reaction a). The monoperoxidovanadate intermediate subsequently combines with peroxide to regenerate the original catalyst in the presence of excess  $H_2O_2$ , thereby completing the catalytic cycle (reaction b).

<Fig. 14>

### 4. Conclusions

To conclude, this report highlights the preparation and characterization of a new peroxidovanadium(V) compound immobilized on chitosan and its use as a cost-effective environmentally safe heterogeneous catalyst for the selective oxidation of sulfides to their respective sulfoxides in aqueous medium. The compatibility of the catalyst in relatively safer organic solvents as well, under mild conditions, to afford desired products with impressive yields, is an additional important attribute of the catalyst. Apart from the high activity and product selectivity displayed in both aqueous as well as organic media, other significant strengths of the protocol which make it attractive from both economic and ecological

perspectives include (i) chemoselectivity and easy recyclability of the catalyst for several catalytic cycles; (ii) high  $H_2O_2$  efficiency percentage; (iii) ready scalability; (iv) simplicity in operation and work-up procedure.

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### **Table Legends**

**Table 1** BET surface area,  $V_{tot}$  and the pore radius of the polymer support, chitosan, andpolymer bound peroxidovanadium complex, **ChpV** 

 Table 2 <sup>13</sup>C NMR spectral data for chitosan and ChpV

Table 3 Thermogravimetric data of the ChpV compound

**Table 4** Optimization of the reaction conditions for the selective oxidation of methyl phenylsulfide (MPS) by 30%  $H_2O_2$ , catalysed by the **ChpV** complex<sup>a</sup>

Table 5 Selective oxidation of sulfides to sulfoxides with 30%  $H_2O_2$  catalysed by ChpV in  $H_2O^a$ 

Table 6 Selective oxidation of sulfides to sulfoxides with 30%  $H_2O_2$  catalysed by ChpV in  $CH_3CN^a$ 

### **Captions for Figures**

Fig. 1 Scanning electron micrographs of (a) chitosan and (b) ChpV. EDX spectrum of (c) ChpV.

Fig. 2 X-ray diffraction (XRD) pattern of (a) chitosan and (b) ChpV.

Fig. 3 XPS spectra of V  $(2p_{3/2})$ , V  $(2p_{1/2})$  and O (1s) peaks for ChpV.

Fig. 4 Adsorption/desorption isotherm of ChpV.

Fig. 5 IR spectra of (a) chitosan and (b) ChpV.

Fig. 6 Raman spectrum of ChpV.

Fig. 7 Electronic spectrum of ChpV.

Fig. 8<sup>13</sup>C NMR spectra of (a) chitosan and (b) ChpV.

Fig. 9<sup>51</sup>V NMR spectrum of ChpV.

Fig. 10 TG-DTG plot of ChpV.

Fig. 11 Proposed structure of ChpV. (\* represents polymer chain)

Fig. 12 Recyclability of ChpV for the selective oxidation of MPS to sulfoxide in H<sub>2</sub>O and CH<sub>3</sub>CN.

Fig. 13 IR spectra of (a) ChpV, (b) ChpV after 3<sup>rd</sup> cycle in H<sub>2</sub>O and (d) ChpV after 5<sup>th</sup> cycle in CH<sub>3</sub>CN.

Fig. 14 The proposed catalytic cycle.

Scheme 1 Synthesis of the pV complex anchored on chitosan (ChpV) (\* represents polymer chain).

Table 1	I BET	surface	area,	$V_{\text{tot}}$	and	the	pore	radius	of	the	polymer	support,	chitosan,	and
polyme	r boun	d peroxic	dovana	adiur	n co	mple	ex, C	hpV						

Compound	$S_{BET}(m^2/g)$	V <sub>tot</sub> (mL/g)	Pore diameter (Å)	
Chitosan	3.0	0.05	32.0	
ChpV	43.6	0.06	38.7	
			50	
IMR spectral da	ata for chitosan	and ChpV		

 Table 2 <sup>13</sup>C NMR spectral data for chitosan and ChpV

Compound	Chemical shift (ppm)									
-	C-1	C-2	C-3C-5	C-4	C-6					
Chitosan	106.3	58.7	76.8	85.1	62.3					
ChpV	100.5	57.7	76.8	85.8	62.7					

### Table 3 Thermogravimetric data of the ChpV compound

Compound	Temperature range	Observed weight loss (%)	Final residue
	(°C)		(%)
	37-65	5.9	
ChpV	139-182	12.7	59.8
	226-310	21.6	

	Í	s_	ChpV		S S		s	~
	لر		Solvent, 30 % H	202	, T			
		1		1a		1b		
Entry	Molar ratio	$H_2O_2$	Solvent	Time	Isolated	1a:1b	TON <sup>b</sup>	$\mathrm{TOF}^{\mathrm{c}}(\mathrm{h}^{-1})$
	(V:MPS)	(equiv.)		(min)	yield (%)			
1	1:1000	2	H <sub>2</sub> O	300	96	100:0	960	192
2	1:1000	3	$H_2O$	180	94	100:0	940	313
3	1:1000	4	$H_2O$	75	96	100:0	960	768
4	1:1000	5	H <sub>2</sub> O	40	98	100:0	980	1462
5	1:1000	6	$H_2O$	25	98	76:24	760	1809
6	1:2000	5	$H_2O$	90	97	100:0	1940	1293
7	1:500	5	$H_2O$	30	95	82:18	410	820
8	1:1000	1	CH <sub>3</sub> CN	120	94	100:0	940	470
9	1:1000	2	CH <sub>3</sub> CN	30	95	100:0	950	1900
10	1:1000	3	CH <sub>3</sub> CN	20	98	89:11	890	2696
11	1:500	2	CH <sub>3</sub> CN	20	96	100:0	480	1454
12	1:1500	2	CH <sub>3</sub> CN	70	97	100:0	1469	1259
13	1:2000	2	CH <sub>3</sub> CN	130	95	100:0	1900	876
14	1:1000	2	MeOH	80	97	100:0	970	729
15	1:1000	2	EtOH	60	97	100:0	970	970
16 <sup>d</sup>	<b>(</b> )-	5	H <sub>2</sub> O	40	11	78:22	-	-
17 <sup>d</sup>	-	2	CH <sub>3</sub> CN	30	9	71:29	-	-
$18^{\rm e}$	1:1000	5	$H_2O$	70	98	92:8	900	771
19 <sup>e</sup>	1:1000	2	CH <sub>3</sub> CN	90	96	81:19	780	520

**Table 4** Optimization of reaction conditions for selective oxidation of methyl phenyl sulfide(MPS) by 30%  $H_2O_2$  catalysed by the **ChpV** complex<sup>a</sup>

<sup>a</sup>All reactions were carried out with 5 mmol of substrate, 30% H<sub>2</sub>O<sub>2</sub> in 5 mL of solvent. Catalyst (2.1 mg for 0.005 mmol of V). <sup>b</sup>TON (turnover number) = mmol of product per mmol of catalyst. <sup>c</sup>TOF (turnover frequency) = mmol of product per mmol of catalyst per hour. <sup>d</sup>Blank experiment without any catalyst. <sup>e</sup>Using DPV as catalyst (0.8 mg, 0.005 mmol).

Table 5 Selective oxidation of sulfides to sulfoxides with 30%  $H_2O_2$  catalysed by ChpV in  $H_2O^a$ 

	S ChpV (V: Sub= 1:1000) 30% H <sub>2</sub> O <sub>2</sub> (5 equivalents), RT, H <sub>2</sub> O										
Entry	Substrate	Mol	ar ratio	Time	Isolated	Sulfoxide:	TON	TOF			
		V:MPS	MPS:H <sub>2</sub> O <sub>2</sub>	(min)	Yield (%)	Sulfone		(h <sup>1</sup> )			
1	S S	1:1000	1:5	40	98	100:0	980	1462			
		1:1000 <sup>b</sup>	1:5	40	96	100:0	960	1432			
		1:1000 <sup>c</sup>	1:5	40	97	100:0	970	1447			
2	∕ <sup>s</sup> ∕	1:1000	1:5	10	94	100:0	940	5628			
3	M <sub>3</sub> <sup>S</sup> M <sub>3</sub>	1:1000	1:5	30	95	100:0	950	1900			
4	$\mathcal{M}_5^{S}\mathcal{M}_5^{S}$	1:1000	1:2	35	96	100:0	960	1646			
5		1:1000	1:5	50	97	100:0	970	1164			
6		1:1000	1:5	35	93	100:0	930	1595			
7	ОН	1:1000	1:5	75	94	100:0	940	752			
8		1:1000	1:5	150	96	100:0	960	384			
9		1:1000	1:5	360	39	100:0	390	65			

<sup>a</sup>All reactions were carried out with 5 mmol substrate, 25mmol 30%  $H_2O_2$  and catalyst (0.005 mmol of V) in 5 mL  $H_2O$  at RT. <sup>b</sup>Yield of 3<sup>rd</sup> reaction cycle. <sup>c</sup>Yield at scale-up reaction (7.5 g of MPS).

Table 6 Selective oxidation of sulfides to sulfoxides with 30%  $H_2O_2$  catalysed by ChpV in  $CH_3CN^a$ 

	$\frac{ChpV (V: Sub= 1:1000)}{30\% H_2O_2 (2 equivalents), RT, CH_3CN}$										
Entry	Substrate	Mol	ar ratio	Time	Isolated	Sulfoxide:	TON	TOF			
		V:MPS	MPS:H <sub>2</sub> O <sub>2</sub>	(min)	Yield (%)	Sulfone		$(h^{-1})$			
1	s S	1:1000	1:2	30	97	100:0	970	1940			
		1:1000 <sup>b</sup>	1:2	30	96	100:0	960	1920			
		1:1000 <sup>c</sup>	1:2	30	93	100:0	930	1860			
2	∕ <sup>s</sup> ∕	1:1000	1:2	10	95	100:0	950	5688			
3	M <sub>3</sub> <sup>S</sup> M <sub>3</sub>	1:1000	1:2	20	94	100:0	940	2848			
4	$\mathcal{M}_5^{S}\mathcal{M}_5$	1:1000	1:2	30	96	100:0	960	1920			
5	S S	1:1000	1:2	70	97	100:0	970	829			
6		1:1000	1:2	25	94	100:0	940	2238			
7	ОН	1:1000	1:2	120	93	100:0	930	465			
8		1:1000	1:2	110	94	100:0	940	513			
9		1:1000	1:2	360	47	100:0	470	78			

<sup>a</sup>All reactions were carried out with 5 mmol substrate, 10 mmol 30%  $H_2O_2$  and catalyst (0.005 mmol of V) in 5 mL acetonitrile at RT. <sup>b</sup>Yield of 5<sup>th</sup> reaction cycle. <sup>c</sup>Yield of scale up reaction (7.5 g of MPS).





Fig. 1



























Scheme 1

