



New polymer-immobilized peroxotungsten compound as an efficient catalyst for selective and mild oxidation of sulfides by hydrogen peroxide

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ABSTRACT

A new polymer-bound peroxotungstate(VI) catalyst of the type $[W(O)_2(O_2)(CN)_2]$ -PAN [PAN=poly(acrylonitrile)] (**PANW**) has been prepared by reacting H_2WO_4 with 30% H_2O_2 and the macromolecular ligand, PAN at pH 5.0. The compound was characterized by elemental analysis, SEM, EDX, TGA and spectral studies (FTIR and ^{13}C NMR). Clean conversion of a variety of sulfides and dibenzothiophene (DBT) to the corresponding sulfoxide or sulfone, using H_2O_2 as oxidant, could be achieved in the presence of the heterogeneous catalyst **PANW**, by a versatile variation of reaction conditions. The reactions proceed under mild conditions to afford the resulting products with impressive turn over frequency (TOF). The catalyst exhibit complete chemoselectivity toward sulfur group of substituted sulfides with other oxidation prone functional groups. Easy regeneration and reusability of the catalyst for at least up to seven catalytic cycles with consistent activity and selectivity is an important attribute of the catalyst.

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1. Introduction

The contemporary interest in the selective oxidation of sulfur containing compounds has to a great extent been fueled by the utility of sulfoxides as fine chemicals, pharmaceuticals and as valuable intermediates for the construction of chemically and biologically active molecules [1–5]. Moreover, oxidative desulfurization processes are emerging as important and sustainable procedures for obtaining ultra low sulfur fuels [6–12].

Aqueous H_2O_2 of less than 60% concentration has been recognized as ideal, clean and green oxidizing agent [13–15] for oxidation of sulfides under acidic conditions [16]. However, owing to its being a mild oxidant the H_2O_2 mediated oxidations are usually very slow and often require to be activated by homogeneous or heterogeneous catalysts [16–18]. This feature has spurred the development of a plethora of useful and interesting catalysts, including vanadium [19–21], rhenium [22], iron [23–25], manganese [26,27], titanium [8,28] and tungsten [16,17,29–36] based systems, for oxidation of sulfides by H_2O_2 . Despite these important progresses, scope for improvement still remains owing to some of the disadvantages associated with the available protocols viz., over oxidation, low TON, high cost, difficulty in regeneration of the catalyst, and requirements such as high temperature, long reaction time,

a promoter or a co-catalyst, chlorohydrocarbon solvents and excessive H_2O_2 , which limit their practical utility. Therefore, search for newer catalysts, active under improved environmentally acceptable conditions, for selective oxidation of sulfide continues unabated.

It is pertinent here to mention that we have recently developed a series of polymer anchored peroxovanadium and peroxomolybdenum compounds [37,38], as well as a set of monomeric and dimeric peroxotungsten (pW) complexes [39–42], a few of which proved to be effective oxidants of bromide with good activity at ambient temperature and neutral pH, an essential requirement of a biomimetic model [38,41]. Also, the compounds efficiently mediated bromination of organic substrates in aqueous organic media [38,41,43]. This finding is significant particularly because, contrary to natural vanadium bromoperoxidases which are most efficient at pH 5.5–7 several model complexes were found to be catalytically active only in acid medium [44–46].

Inspired by the above observations, in the present work, we endeavored to generate polymer supported peroxotungsten compound with an ability to serve as heterogeneous catalyst for selective oxidation of organic sulfide to sulfoxide or sulfone, under mild reaction conditions. Peroxotungsten complexes (pW) have been receiving continued attention mainly owing to their applications as efficient and versatile catalysts in a variety of organic oxidations [6,13,34,47–51] including sulfide oxidation [6,13,48,49]. Much of the stimulations for research in the area of polymer-anchored catalytically active transition metal complexes have come from the advantages associated with converting selective homogeneous catalysts to heterogeneous polymer supported

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systems, including enhancement of stability, easy work up of reaction mixture, regeneration and reusability of such systems [52–54]. Polymer-immobilized peroxometallates are yet to be fully explored for their potential as environmentally benign heterogeneous catalysts in organic oxidations. A few peroxometal systems supported on insoluble cross-linked polymers were reported recently which were found to exhibit good activity as catalytic or stoichiometric oxidant in organic oxidations [55–58]. Proper choice of the functional group is an important prerequisite in order to obtain a stable polymer–metal linkage [38,52,54]. Further, the task of establishing a robust polymer–metal bond which will be retained after repeated catalytic cycles is particularly challenging in the regeneration of supported catalytic species [52,56,58].

Here, we present the preparation and characterization of a new polymer-bound pW compound, prepared by incorporating peroxotungsten species into the poly(acrylonitrile) matrix (PAN), and its activity as a heterogeneous catalyst in selective oxidation of thioethers and dibenzothiophene (DBT) by H₂O₂, to the corresponding sulfoxide or sulfone. We selected PAN as a suitable support for the purpose of this investigation due to its being a non-toxic, cheap and commercially available reagent. Most importantly, it provides suitable pendant functional groups for easy attachment of transition metals [59,60]. In addition, acrylonitrile polymers have attracted much attention for their application in diverse areas that include medicine [61], antioxidants [61], surface coatings [62], catalysis [60], textiles treatment [61], binders [61] and as adsorbant for removal of heavy metal ions from water [59,63].

2. Experimental

2.1. Materials

The chemicals used were all reagent grade products. The sources of chemicals are given below: Tungstic acid (Himedia laboratories, Mumbai, India), acetone, hydrogen peroxide, acetonitrile, methanol, ethylacetate, petroleum ether, diethyl ether, dichloromethane (RANKEM), silica gel (60–120 mesh), sodium hydroxide, sodium sulfate (E. Merck, India). The poly(acrylonitrile) (PAN) (Mw = 48,200), methyl phenyl sulfide (MPS), dimethyl sulfide (DMS), dibutyl sulfide (DBS), butyl propyl sulfide (BPS), dibenzothiophene (DBT), phenylvinyl sulfide (PVS), 2-(phenylthio)ethanol (PTE) 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 [WO₂(O₂)(CN)₂]-PAN [PAN = poly(acrylonitrile)] (PANW)

In a typical reaction, 1.17 g of H₂WO₄ (4.72 mmol) was dissolved in minimum volume of H₂O₂ (30% solution, 10 mL) in a 250 mL beaker with constant stirring at room temperature. The pH of the clear solution obtained was recorded to be 1.21. Concentrated sodium hydroxide (ca. 8 M) was then added to the above solution dropwise with constant stirring to raise the pH of the reaction medium to 5.0. Keeping the temperature of the reaction mixture below 4 °C in an ice bath, 1.0 g of poly(acrylonitrile) was added to it. The suspended polymer beads were allowed to swell in the reaction mixture under continuous stirring for 24 h. The supernatant liquid was then decanted and the white residue was repeatedly washed with pre-cooled acetone. The product was separated by centrifugation and dried in vacuo over concentrated sulfuric acid.

Found: C, 63.41; H, 2.86; N, 25.37; W, 6.84; O₂²⁻, 1.20%. The metal loading calculated from the observed tungsten content is 0.38 mmol g⁻¹ of polymer for [WO₂(O₂)(CN)₂]-PAN.

2.3. Elemental analysis

The compounds were analyzed for C, H and N by using elemental analyzer Perkin Elmer 2400 series II. Tungsten content was determined by EDX analysis as well as by gravimetric estimation as BaWO₄. Peroxide content was determined by adding a weighed amount of the compound to a cold solution of 1.5% boric acid (w/v) in 0.7 M sulfuric acid (100 mL) and titration with standard Cerium(IV) solution [64].

2.4. Physical and spectroscopic measurements

The IR spectra were recorded with samples as KBr pellets in a Nicolet model 410 FTIR spectrophotometer. The spectra were recorded at ambient temperature by making pressed pellets of the compounds. Spectra in the visible and ultraviolet region were recorded in a Cary 100 Bio, Varian spectrophotometer equipped with a peltier controlled constant temperature cell. Thermogravimetric analysis was done in SHIMADZU TGA-50 system at a heating rate of 10 °C/min under an atmosphere of nitrogen using aluminum pan. The SEM characterization was carried out using the JEOL JSM-6390LV Scanning Electron Micrograph attached with an energy-dispersive X-ray detector. Scanning was done at 1–20 μm range and images were taken at a magnification of 15–20 kV. Data were obtained using INCA software. The standardization of the data analysis is an integral part of SEM-EDX instrument employed. The ¹³C NMR spectra for PAN and PANW were recorded in a JEOL JNM-ECS400 spectrometer at carbon frequency 100.5 MHz, 32,768 X-resolution points, number of scans 10,000, 1.04 s of acquisition time and 2.0 s of relaxation delay with ¹H NMR decoupling method in DMSO-*d* + DMF (1:4). The ¹H and ¹³C NMR of organic sulfides, sulfoxides and sulfones were recorded in a JEOL JNM-ECS400 spectrometer (CDCl₃ as solvent and TMS as an internal standard). Melting points were determined in open capillary tubes on a Büchi Melting Point B-540 apparatus and are uncorrected. GC analysis was carried out on a CIC, Gas Chromatograph model 2010 using a SE-52 packed column (length 2 m, 1/8 in. OD) with a Flame Ionization Detector (FID), and nitrogen as carrier gas (30 mL/min).

2.5. General procedure for oxidation of sulfides to sulfoxides

In a representative procedure, organic substrate (5 mmol) was added to a mixture of PANW (13.2 mg, containing 0.005 mmol of W) and 30% H₂O₂ (1.13 mL, 10 mmol) in methanol (5 mL), maintaining molar ratio of W:substrate at 1:1000 and substrate:H₂O₂ at 1:2, in a 50 mL two-necked round-bottomed flask. The reaction was conducted at room temperature (RT) under continuous 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 as well as unreacted organic substrates were extracted with diethyl ether from the filtrate and dried over anhydrous Na₂SO₄ and distilled under reduced pressure to remove excess diethyl ether. The corresponding sulfoxide obtained was purified by column chromatography on silica gel using ethyl acetate and *n*-hexane (1:9).

The products obtained were characterized by IR, ¹H NMR, ¹³C NMR spectroscopy and in case of solid sulfoxide products, in addition to the above spectral analysis, we have carried out melting point determination (see Supporting Information).

2.6. General procedure for oxidation of sulfides to sulfones

To a stirred solution of sulfide (5 mmol) in acetonitrile (5 mL), 50% H₂O₂ (1.36 mL, 20 mmol) and the catalyst (13.2 mg, containing 0.005 mmol of W) were added successively maintaining molar ratio of W:substrate at 1:1000 and substrate:H₂O₂ at 1:4. The resulting

reaction mixture was stirred at room temperature. After completion of the reaction, the sulfone obtained was isolated, purified and characterized by methods similar to those mentioned under procedure for oxidation of sulfide to sulfoxide (Section 2.5).

2.7. Regeneration of the catalyst

The regeneration of the catalyst for reuse was tested for the reaction using methyl phenyl sulfide (MPS) as substrate. Since we have optimized two types of reaction conditions for selective transformation of sulfide to sulfoxide or sulfone, the recyclability of the reagent was examined for the afore mentioned reactions separately. In the sulfoxidation reaction, the reaction mixture contained the same recipe mentioned under Section 2.5. The catalyst was separated by centrifugation after being used in the reaction (35 min) washed in acetone and dried in vacuo over concentrated sulfuric acid. The catalyst was then placed into a fresh reaction mixture containing 30% H₂O₂ (1.13 mL, 10 mmol), substrate (5 mmol) and methanol (5 mL). The progress of the reaction was monitored by thin layer chromatography (TLC) and GC.

In case of the reaction of oxidation of MPS to sulfone, the separated catalyst after completion of the reaction (90 min) was similarly subjected to further catalytic cycle by placing it into a fresh reaction mixture of 50% H₂O₂ (1.36 mL, 20 mmol), MPS (5 mmol) and acetonitrile (5 mL) as mentioned under Section 2.6.

In an alternative procedure, regeneration of the spent catalyst was achieved by charging the spent reaction mixture, remaining in the reaction vessel after separating the organic reaction product, with fresh H₂O₂ and substrate and then repeating the experiment. Each of the procedures was repeated for seven cycles.

3. Results and discussion

3.1. Synthesis

In the present work the anchoring of peroxotungsten species to the poly(acrylonitrile) matrix to obtain the heterogeneous catalyst **PANW**, could be achieved easily by stirring the mixture containing the polymer and peroxotungsten species, generated in situ by reacting H₂WO₄ with H₂O₂ at pH ca. 5, in an ice-bath for ca. 24 h. The strategically maintained pH of ca. 5 was found to be optimal for the desired synthesis of the polymer anchored pW compound. An essential component of the procedure is to limit water to that contributed by 30% H₂O₂ and alkali hydroxide solution. The catalyst is stable, non-hygroscopic and can be stored for a prolonged period without any change in its catalytic efficiency.

3.2. Characterization

The elemental analysis data for the compound indicated the presence of one peroxide group per metal center. The tungsten loading on the compound calculated on the basis of tungsten content obtained from chemical analysis as well as EDX analysis was found to be 0.38 mmol per gram of the polymeric support.

Scanning electron microscopy was employed to study the particle size as well as morphological changes occurring on the surface of the polymer after loading of the peroxotungstate to the polymer matrix. The SEM micrographs revealed that the metal ions are distributed across the surface of the polymer in **PANW**. The average particle size of the pristine PAN beads was recorded to be 1.85 μm (Fig. 1(A)). The SEM micrograph of the catalyst (Fig. 1(B)) showed considerable enhancement of the average particle size after incorporation of pW moieties into the PAN matrix. Energy dispersive X-ray spectroscopy of the compounds, which provides in situ chemical analysis of the bulk, clearly showed W, C, N and O as the constituents of the anchored complexes. The absence of sodium as

Table 1
Infrared spectral data for **PANW**.

PANW	Assignment
535(m)	$\nu_{sym}(W-O_2)$
611(m)	$\nu_{asym}(W-O_2)$
858(m)	$\nu(O-O)$
939(m)	$\nu(W=O)$
2247(vs)	$\nu(C\equiv N)$
2366(m)	
2867(m)	$\nu_{sym}(CH_2)$
2937(m)	$\nu_{asym}(CH_2)$

counter ion in the compound indicated the charge neutrality of the nitrile bound monoperoxotungsten(VI) species, consistent with the formula assigned. The EDX spectral data obtained on the composition of the compound were in good agreement with the elemental analysis values.

3.2.1. IR and electronic spectral studies

The significant features of IR spectrum of the polymer-anchored peroxy complex **PANW** are summarized in Table 1 and presented in Fig. 2. The presence of side-on bound peroxy ligand in the compound was evident from the observance of the characteristic $\nu(O-O)$, $\nu_{asym}(W-O_2)$ and $\nu_{sym}(W-O_2)$ modes in the vicinity of ca. 860, ca. 610 and ca. 530 cm⁻¹, respectively [65,66]. The strong absorption at ca. 940 cm⁻¹ have been assigned to $\nu(W=O)$ mode of terminally bonded W=O group [65,66].

By comparison of IR spectrum of the anchored complex to the spectrum of pure poly(acrylonitrile) [67] and the available literature data on metal compounds with co-ordination environment comprising nitrile ligand as well as PAN [60,68,69], fairly reliable empirical assignments could be derived for the IR bands observed for **PANW**. The pristine polymer has a strong $\nu(C\equiv N)$ absorption at 2247 cm⁻¹, apart from the characteristic bands at 2937 and 2867 cm⁻¹ due to $\nu_{asym}(CH_2)$, $\nu_{sym}(CH_2)$, respectively (Fig. 2). The spectrum of the compound after incorporation of pW species displayed, in addition to the band at 2247 cm⁻¹ for the free nitrile groups, a new medium intensity band at 2366 cm⁻¹. This latter band is attributable to a shift of $\nu(C\equiv N)$ to a higher frequency, resulting from co-ordination of the W(VI) ion with the pendant nitrile group of the polymer. It has been documented that in simple N-bonded nitrile complexes there is usually an increase in $\nu(C\equiv N)$ upon coordination [60,68,69].

A band has been expected in the electronic spectra of the **PANW** in the range of 320–330 nm, attributable to LMCT transitions originating from co-ordinated peroxide of monoperoxy derivatives of tungsten [70,71]. However, no such peak was observed in the spectrum of the catalyst probably due to the low metal loading on the polymer matrix.

3.2.2. ¹³C NMR studies

The study of co-ordination induced ¹³C NMR chemical shift has been recognized as an important tool in understanding the mode of coordination of the co-ligands in peroxy metal compounds [37,66,72–76]. The ¹³C NMR spectra of the pure PAN polymer displays resonance due to pendant nitrile group at 120.21 ppm and the characteristic signals corresponding to chain carbon atoms at 33.35 (for CH₂) and 27.97 (for CH) ppm. The assignments are on the basis of the available literature data [77]. The spectrum of **PANW**

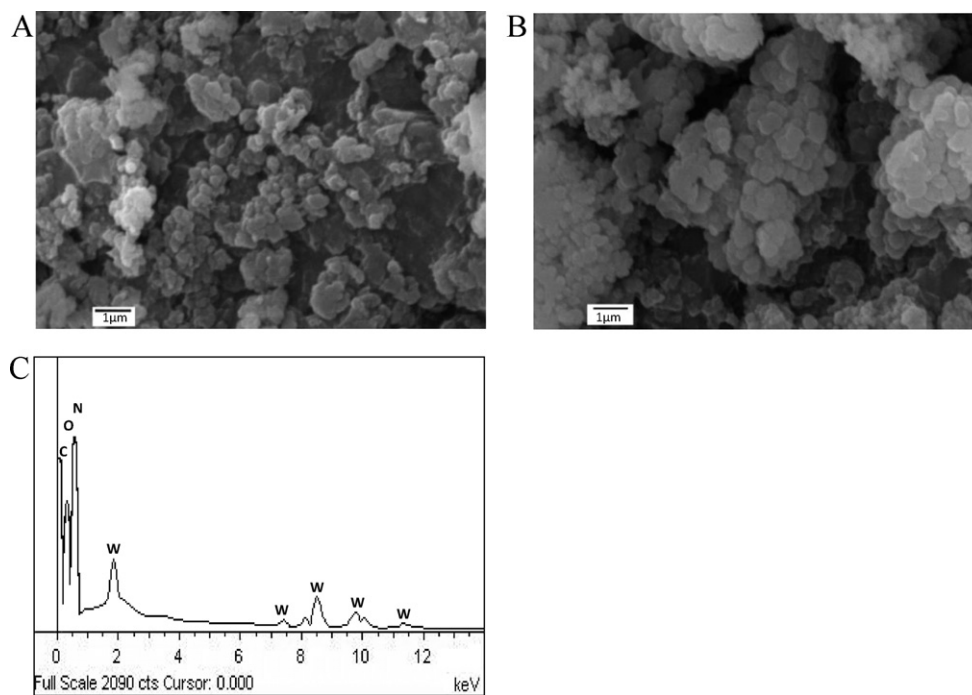


Fig. 1. Scanning electron micrographs of (A) PAN and (B) PANW. EDX spectra of (C) PANW.

exhibited a new signal at 128.48 ppm attributable to tungsten bound nitrile group in addition to the signal at δ 120.15 ppm owing to free nitrile group of the polymer (Fig. 3). It has been documented that on co-ordination to a metal the nitrile carbon resonance undergoes a downfield shift [78]. The spectrum of PANW thus evidenced for the presence of both coordinated and free nitrile groups. The substantial downfield shift, $\Delta\delta$ ($\delta_{\text{complexed nitrile}} - \delta_{\text{free nitrile}}$) \approx 8 ppm

in the metal anchored compound relative to the free nitrile peak of the pristine polymer suggests strong metal–ligand interaction. The findings from the ^{13}C NMR spectral analysis of the compound is consistent with retention of its solid-state structure in solution.

3.2.3. Thermal analysis

The TG–DTG plots for the compound PANW presented in Fig. 4 shows that the compound undergoes multistage decomposition on heating up to a temperature of 750 °C. It is noteworthy that unlike pure PAN or some monomeric peroxometal compounds [79], the polymer-anchored catalyst does not explode on heating and remains stable up to a temperature of 115 °C. The degradation of PAN in the temperature range 250–400 °C has been reported to be explosive in nature [67]. In PANW, the first stage

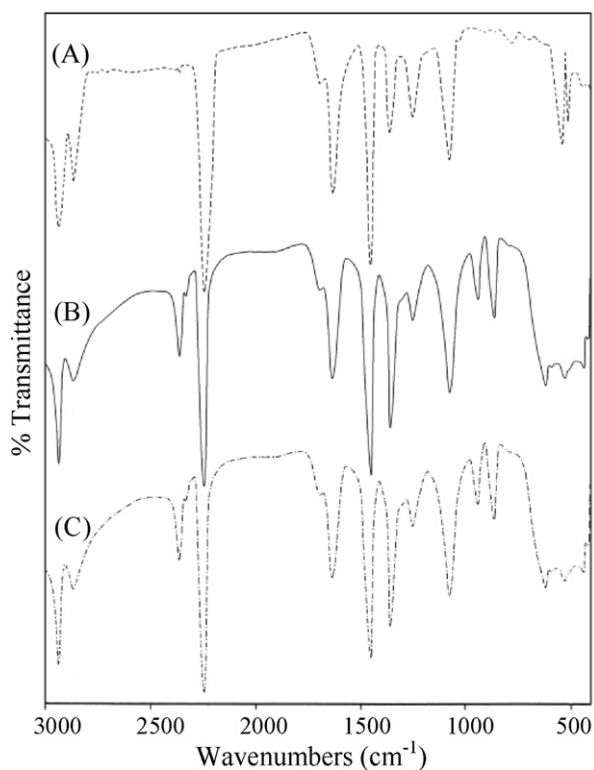


Fig. 2. FTIR spectra of (A) PAN, (B) PANW and (C) PANW after 7th cycle of reaction.

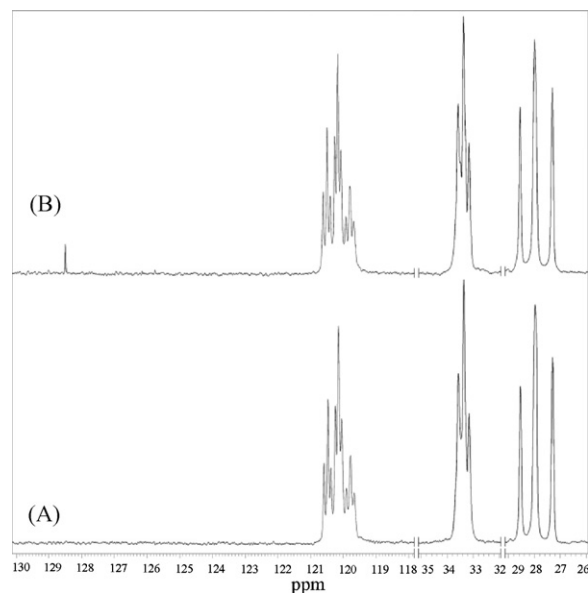


Fig. 3. ^{13}C NMR of (A) PAN and (B) PANW in DMSO- d_6 + DMF (1:4).

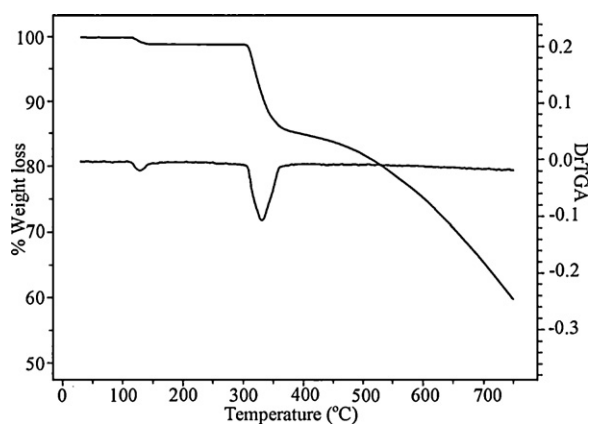


Fig. 4. TG–DTG plot of PANW.

decomposition occur in the temperature range of 115–141 °C with the corresponding weight loss of 1.21%, attributable to loss of peroxide ligand. The absence of peroxide in the decomposition product, isolated at this stage, was confirmed from the IR spectral analysis. The next decomposition occurred between 305 and 360 °C which appeared as a single peak in DTG (weight loss 12.83%). The degradation further continued up to 750 °C. IR spectrum of the residue obtained at 360 °C showed bands at 1578 cm^{-1} and 1625 cm^{-1} characteristic of $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ stretching in addition to $\nu(\text{W}=\text{O})$ at 957 cm^{-1} . The results are in general agreement with previous work where it was found that the degradation of PAN below 400 °C is accompanied by elimination of HCN, NH_3 and H_2O and concomitant intramolecular polymerization of nitrile groups to form conjugated polyamine $(-\text{C}=\text{N})_n$ and that the loss of nitrogen commences at 750 °C [80]. The total weight loss which occurred during the course of the overall decomposition process on heating the compound up to a final temperature of 750 °C was recorded to be 59.82%. Thermogravimetric analysis data of the compound thus provided further evidence in support of its composition and formula assigned.

Based on the above data, a structure of the type shown in Fig. 5, has been proposed for the compound PANW which includes tungsten(VI) atom with a side-on bound peroxy and terminal $\text{W}=\text{O}$ groups, bonded to the polymer matrix via the pendant nitrile groups. Simultaneous bond formation of $\text{W}(\text{VI})$ to the two neighboring nitrile groups of the polymer chain appears to complete the hexa co-ordination around each tungsten atom.

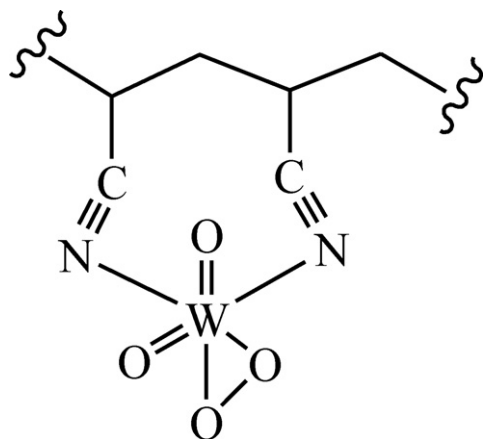


Fig. 5. Proposed structure of PANW. “*wavy*” represents polymer chain.

3.3. Catalytic activity of PANW

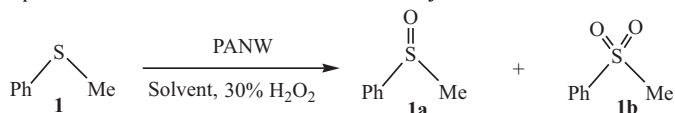
3.3.1. Oxidation of sulfides to sulfoxides

The efficacy of the polymer-immobilized pW compound, PANW as catalyst in the oxidation of organic sulfides, using H_2O_2 as terminal oxidant, has been explored. In order to optimize the reaction conditions, several reaction runs were performed using methyl phenyl sulfide (MPS) as model substrate (S) in the presence of different solvents as shown in Table 2.

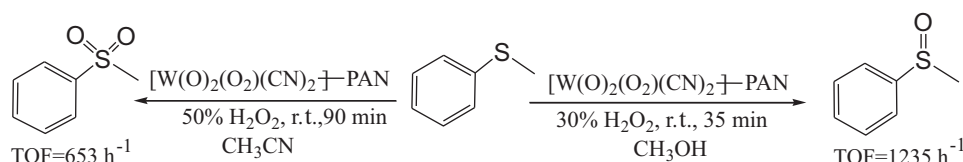
The reactions were conducted at room temperature (r.t.) under magnetic stirring. In a preliminary experiment, MPS was allowed to react with H_2O_2 (1 equiv.) maintaining the W:substrate molar ratio at 1:1000 in methanol. Under these conditions MPS has been rapidly oxidized initially to sulfoxide and then to sulfone to afford ultimately a mixture of **1a** and **1b** in the ratio of 77:23 (Table 2, entry 1). The initial fast reaction was observed to slow down on prolonged reaction time and remained incomplete even after 5 h. The significant finding of the reaction run was the facile formation of sulfoxide as the exclusive product within the initial period of ca. 30 min of starting the reaction. The observation led us to examine the possibility of achieving selective sulfoxidation of MPS by terminating the reaction at specific time after the initial formation of sulfoxide in order to prevent over oxidation to sulfone. Indeed, when a reaction carried out separately under analogous condition was terminated after 35 min of its starting, pure sulfoxide could be isolated in ca. 49% yield (Table 2, entry 2). The yield of **1a** could be improved further to nearly 72% by increasing the amount of H_2O_2 to 2 equiv., leading to reasonably high TOF (Table 2, entry 3). A 1:2 molar ratio of oxidant:substrate, thus appeared to be optimal in order to achieve high TOF without affecting the selectivity. Allowing a similar reaction to run for 50 min although led to complete conversion of sulfide with a nearly 97% isolated product yield (Table 2, entry 4), however, 16–20% of sulfone was also formed along with sulfoxide, thereby reducing the selectivity of the oxidation. The data obtained thus evidenced for higher selectivity at lower conversions. The effect of catalyst amount was then evaluated (Table 2, entries 5 and 6). A 5 or 10-fold increase in the amount of catalyst, albeit led to an enhancement in the rate of the reaction. However, the corresponding TOF was found to decrease. We have therefore decided to maintain a W:S molar ratio at 1:1000 for subsequent reactions.

The nature of the solvent was found to play a crucial role in determining the activity and selectivity of the catalyst in the oxidation reactions. We were particularly interested to carry out the reactions in environmentally acceptable common organic solvents as well as in water. The data in Table 2 clearly shows that both methanol and ethanol, fully miscible with the organic substrate and H_2O_2 , are highly effective as a solvent affording product selectivity as well as high TOF in the presence of the catalyst. The results also indicated a favorable effect of the protic solvent. The observation is in agreement with previous report that solvents of high hydrogen bonding ability favor the formation of sulfoxide with high chemoselectivity [20,24,81]. No appreciable conversion was noted in aqueous medium in the present case probably due to the insolubility of the catalyst as well as the substrate in water. Reactions were also conducted in solvents such as chloroform or dichloromethane which yielded low conversions of MPS within the range of 7–11% after 2 h of reaction time. It is interesting to note that when the reaction was conducted in acetonitrile under analogous condition, the concomitant formation of the corresponding sulfone was observed along with sulfoxide (Table 2, entries 8 and 9). Therefore, selective sulfoxidation of MPS could not be attained in acetonitrile even by stopping the reaction at lower conversion.

It is noteworthy that on increasing the reaction temperature up to 65 °C, a 3 to 4-fold increase in TOF could be achieved without affecting the selectivity (Table 2, entries 10 and 11). This striking

Table 2Optimization of reaction conditions for PANW catalyzed selective oxidation of methyl phenyl sulfide (MPS) by 30% H₂O₂.^a

Entry	Molar ratio W:MPS	H ₂ O ₂ (equiv.)	Solvent	Temperature	Time (min)	Isolated yield (%)	1a:1b	TOF (h ⁻¹)
1	1:1000	1	MeOH	r.t.	300	79	77:23	158
2	1:1000	1	MeOH	r.t.	35	49	100:0	840
3	1:1000	2	MeOH	r.t.	35	72	100:0	1235
4	1:1000	2	MeOH	r.t.	50	97	84:16	1164
5	1:500	2	MeOH	r.t.	20	73	100:0	1095
6	1:100	2	MeOH	r.t.	10	71	100:0	426
7	1:1000	2	EtOH	r.t.	35	70	100:0	1200
8	1:1000	2	MeCN	r.t.	120	96	46:54	480
9	1:1000	2	MeCN	r.t.	45	67	75:25	893
10	1:1000	2	MeOH	50 °C	15	73	100:0	2920
11	1:1000	2	MeOH	65 °C	10	74	100:0	4440

^a All reactions were carried out with 5 mmol of substrate in 5 mL of solvent.**Scheme 1.**

feature of the protocol indicated its synthetic utility. In a control experiment conducted in the absence of the catalyst, very little conversion of MPS to sulfoxide or sulfone was observed (<10%) under similar reaction condition. It is thus evident that the catalyst plays a crucial role in facilitating the desired reactions.

Having optimized the right conditions for sulfoxidation (see Scheme 1), a series of various types of structurally diverse sulfides were subjected to the oxidation reaction using PANW–H₂O₂ system. Aliphatic and aromatic sulfides as well as DBT underwent clean and selective oxidation to the corresponding sulfoxide under the optimum condition, in impressive yields and TOFs. The results are summarized in Table 3. Significantly, the maximum selectivity of 100% was achieved at 70–75% of conversion for the substrates (Table 3, entries 1–8).

Termination of the reactions at these conversions thus afforded sulfoxides of high purity. It is pertinent to mention here that no trace of sulfone was detected in the isolated products at this stage of the reactions. The conversion:selectivity as a function of time was investigated for each of the substrates (see Supporting Information Table S1). Although increased conversions were noted with increasing reaction time for each of the substrates tested however, the selectivity was found to be reduced due to the expected overoxidation to sulfone. The observation is consistent with the earlier findings of Choudary et al. [32] pertaining to activity of a W based LDH catalyst in sulfide oxidation.

The rate of the oxidation of thioethers were observed to vary depending on the nature of the substrates and the substituents attached (Table 3, entries 1–8). Allylic and vinylic sulfides (Table 3, entries 5 and 6) were found to be less readily oxidized by H₂O₂ than the dialkyl sulfides probably due to effect of conjugation. These observations are in agreement with the earlier findings that rate of oxidation of sulfides by H₂O₂ increases with the increased nucleophilicity of the sulfide [32,35]. The present protocol is also effective for much less nucleophilic sulfide, such as DBT. Significantly, selective oxidation of DBT, a refractory sulfide, to sulfoxide has been reported to be difficult to achieve with most of the available reaction procedures [11,13,35,82]. In the present work a moderately higher temperature of 65 °C was required to be

employed in case of DBT oxidation since the reaction was relatively sluggish at room temperature. Also, a higher amount of catalyst used (W:substrate ratio of 1:100) further enhanced the rate of the reaction (Table 3, entry 8).

The catalyst exhibited excellent chemoselectivity toward sulfur group of substituted sulfides containing other oxidation prone functional groups such as –C=C– and –OH (Table 3, entries 5–7). Allylic and vinylic sulfoxides were obtained without epoxidation products under such conditions. It is pertinent to highlight herein that the methodology worked well for a relatively larger scale oxidation using 5 g of MPS to give sulfoxide (Table 3, entry 1^e) in high yields, proving its potential for scaled-up synthetic applications.

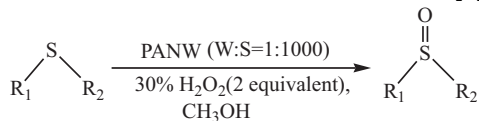
3.3.2. Oxidation of sulfides to sulfones

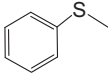
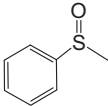
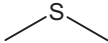
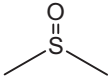
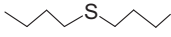
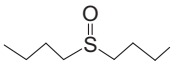
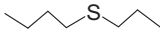
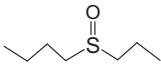
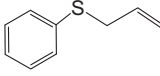
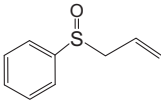
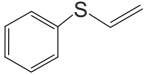
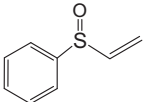
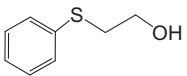
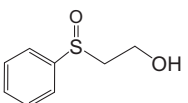
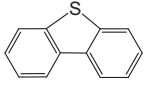
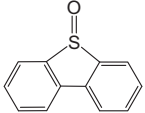
We have observed that formation of sulfone is favored along with sulfoxide when oxidation of MPS was carried out in acetonitrile (Table 2, entries 8 and 9). We have therefore decided to explore the possibility of achieving selective oxidation of sulfides to sulfones by conducting the reaction in acetonitrile. Our initial attempts to obtain pure sulfone using MPS as a model substrate were however, unsuccessful when we used 30% H₂O₂ as the oxidant. Even at a high S:oxidant molar ratio of 1:5 a mixture of 1a and 1b were obtained. On the other hand, clean conversion to sulfone could be achieved for MPS, in excellent yield, and at room temperature within a reasonably short reaction time by using 50% H₂O₂ and maintaining the W:S ratio at 1:1000. It is evident from the data presented in Table 4 that the selectivity toward sulfone gradually increases with increasing concentration of H₂O₂. A substrate:oxidant molar ratio of 1:4 was optimum for the complete conversion of MPS into sulfone under the reaction conditions used (Table 4, entry 4). Apart from MPS, the protocol was also found to be effective for wide range of aromatic and aliphatic substrates, the latter being more reactive as expected. The results are summarized in Table 5.

Most importantly, the TOF of the conversions could be substantially increased by carrying out the reactions under reflux at 78 °C. Even under such relatively drastic conditions viz., the

Table 3

Selective oxidation of sulfides to sulfoxides with 30% H₂O₂ using PANW as catalyst^a at room temperature or 65 °C^b (values within parenthesis).



Entry	Substrate	Time (min)	Product	Isolated yield (%)	TOF ^c (h ⁻¹)
1		35 (10)		72 (74)	1235 (4440)
		35 (10) ^d		69 (72)	1182 (4320)
		35 (10) ^e		73 (70)	1251 (4200)
2		30		71	1420
3		30 (10)		72 (75)	1440 (4500)
4		30 (10)		68 (74)	1360 (4440)
5		45 (12)		65 (70)	866 (3500)
6		180 (55)		76 (74)	253 (807)
7		70 (20)		74 (76)	634 (2280)
8 ^f		(420)		(71)	(10)

^a Reaction conditions: substrate (5 mmol), catalyst (13.2 mg, 0.005 mmol of W), 30% H₂O₂ (1.13 mL, 10 mmol), methanol (5 mL).

^b Reaction at 65 °C in refluxing methanol.

^c TOF (Turnover frequency) = mmol of product per mmol of catalyst per hour.

^d Yield of 7th reaction cycle.

^e Yield at 5 g scale.

^f Substrate (5 mmol), catalyst (132 mg, 0.05 mmol of W), methanol (5 mL).

Table 4

Optimization of reaction conditions for PANW catalyzed selective oxidation of methyl phenyl sulfide (MPS) to sulfone by 50% H₂O₂.^a

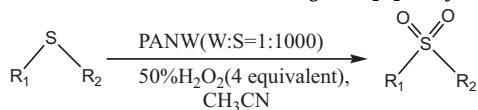
Entry	Molar ratio W:MPS	H ₂ O ₂ (equiv.)	Solvent	Temperature	Time (min)	Isolated yield (%)	1a:1b	TOF (h ⁻¹)
1	1:1000	1	MeCN	r.t.	240	55	46:54	137
2	1:1000	2	MeCN	r.t.	180	97	37:63	323
3	1:1000	3	MeCN	r.t.	120	96	13:87	480
4	1:1000	4	MeCN	r.t.	90	98	0:100	653
5	1:500	4	MeCN	r.t.	60	99	0:100	495
6	1:100	4	MeCN	r.t.	40	97	0:100	145
7	1:1000	4	MeCN	78 °C	25	96	0:100	2304

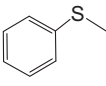
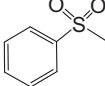
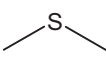
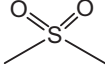
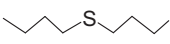
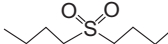
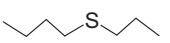
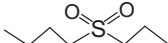
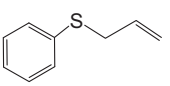
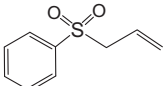
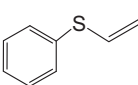
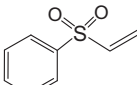
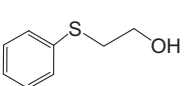
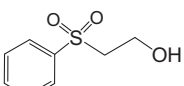
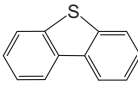
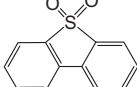
^a All reactions were carried out with 5 mmol of substrate in 5 mL of solvent.

presence of reasonable excess of 50% H₂O₂ and high temperature, the co-existing alcohol and olefinic moieties in substituted sulfides remained unaffected (Table 5, entries 5–7). The results presented in Table 5 show that the oxidation of sulfides to the corresponding sulfones has been achieved with complete chemoselectivity (Table 5, entries 5–7). The suitability of the methodology for scaled up synthesis was also ascertained by conducting the reaction at a 5 g scale (Table 5, entry 1^e).

3.3.3. Catalyst recycling

The recyclability of the catalyst was assessed by using MPS as the substrate. The catalyst afforded regeneration and could be reused without further conditioning after separating the oxidized product and unreacted sulfide from the reaction mixture. The regeneration was accomplished by charging the spent catalyst with H₂O₂, a fresh lot of substrate and the respective solvent after each cycle of reaction. The catalyst was reused for up to seven catalytic cycles.

Table 5Oxidation of sulfides to sulfones using 50% H₂O₂ catalyzed by PANW^a at room temperature or 78 °C^b (values within parenthesis).

Entry	Substrate	Time (min)	Product	Isolated yield (%)	TOF ^c (h ⁻¹)
1		90 (25)		98 (96)	653 (2304)
		90 (25) ^d		93 (91)	620 (2184)
		90 (25) ^e		94 (97)	626 (2328)
2		72		96	800
3		85 (25)		97 (98)	684 (2352)
4		85 (25)		95 (97)	670 (2328)
5		100 (30)		96 (98)	576 (1960)
6		360 (130)		95 (97)	158 (447)
7		270 (80)		96 (98)	213 (735)
8 ^f		(570)		(93)	(9)

^a Reaction conditions: substrate (5 mmol), catalyst (13.2 mg, 0.005 mmol of W), 50% H₂O₂ (1.36 mL, 20 mmol), acetonitrile (5 mL).^b Reaction at 78 °C in refluxing acetonitrile.^c TOF (Turnover frequency) = mmol of product per mmol of catalyst per hour.^d Yield of 7th reaction cycle.^e Yield at 5 g scale.^f Substrate (5 mmol), catalyst (132 mg, 0.05 mmol of W), acetonitrile (5 mL).

Data presented in Table 3 (entry 1^d) and Table 5 (entry 1^d) show that catalyst remain effective with consistent activity and selectivity even after seventh cycle of oxidation. The IR spectrum of the spent catalyst resembled closely the corresponding spectrum of the original starting complex showing the presence of peroxo group, terminal oxo and co-ordinated as well as free nitrile groups indicating that tungsten centers are intact and the coordination environments were not altered during the catalytic process (Fig. 2(C)). Although a slight loss in peroxide content was noted, however, the EDX analysis showed no significant decrease in the metal loading value of the spent catalyst compared to the original catalyst. These findings further indicate that the catalyst PANW remains stable after several cycles of oxidations.

It is important to note that the overall TOF after seven catalytic cycles of oxidation of MPS was recorded to be 8671 h⁻¹ and 4431 h⁻¹ for sulfoxide and sulfone, respectively, at room temperature. These values could further be increased to 30,300 h⁻¹ (for sulfoxide) and 15,792 h⁻¹ (for sulfone) by increasing the reaction temperature (Table 3, entry 1^d and Table 5, entry 1^d). A perusal of the available literature revealed that polymer supported catalyst PANW displayed superior activity in terms of TOF as well as selectivity, achieved under mild reaction condition, over majority

of tungsten containing catalysts reported so far for sulfide oxidation [6,13,16,17,29–36,49].

3.3.4. Test for heterogeneity of the reaction

In order to examine the leaching of the metal complex from the polymer-bound catalyst into the reaction medium during the oxidation reactions, separate experiments were carried out using MPS as the substrate. After completion of the reaction, the catalyst was separated by filtration. The filtrate collected was transferred to a reaction vessel and the reaction was allowed to continue for another 2 h, by adding a fresh MPS–H₂O₂ mixture. In the absence of the catalyst, under analogous conditions the sulfide conversion was noted to be ca. 5%, in line with the value obtained in the absence of any catalyst. This demonstrates that the reaction did not proceed on the removal of the solid catalyst. These data are in agreement with the absence of catalyst leaching and the occurrence of a purely heterogeneous catalytic process.

3.3.5. The proposed mechanism

A scheme of reactions, shown in Fig. 6, is proposed which satisfactorily describes the principal features of our results. It is plausible that the polymer-bound monoperoxotungsten species I reacts with

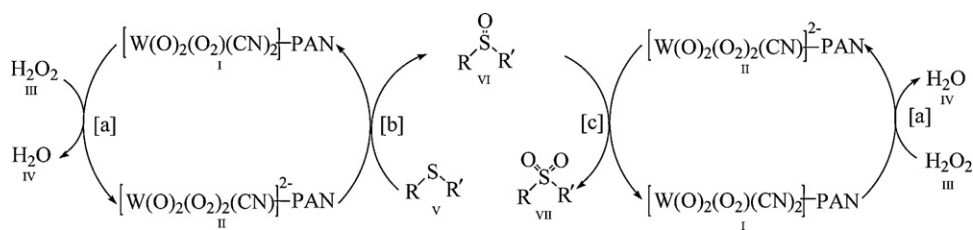


Fig. 6. The proposed mechanism. (a) The polymer-bound monoperoxotungsten species **I** reacts with H_2O_2 to yield the reactive diperoxotungsten intermediate **II**. (b) Transfer of electrophilic oxygen from **II** to the substrate **V** takes place to yield sulfoxide **VI** with concomitant regeneration of the original catalyst **I**. (c) The sulfoxide **VI** may further react with active diperoxotungstate species **II** leading to the formation of sulfone **VII** and simultaneous regeneration of the original catalyst **I**.

H_2O_2 to yield the reactive diperoxotungsten intermediate **II** (reaction a). The electrophilicity of peroxotungstate intermediate being much higher than that of H_2O_2 [33], it is reasonable to expect that facile transfer of electrophilic oxygen to the substrate **V** would take place to yield sulfoxide **VI** (reaction b) with concomitant regeneration of the original monoperoxo W(VI) catalyst **I**. The sulfoxide may further react with the active diperoxotungstate species **II** (reaction c) generated from another cycle of reaction between catalyst **I** and H_2O_2 (reaction a) to yield sulfone. The reaction leading to the formation of sulfone thus appears to be a typical two step process. The facile oxidation of nucleophilic sulfide to sulfoxide is apparently an easier process than the second oxidation of the resulting less nucleophilic sulfoxide to sulfone [32,33]. Although further studies are necessary to establish the exact identity of the reactive diperoxotungsten(VI) species **II**, support for the proposed mechanism comes from the earlier findings that, for a peroxotungstate species to be catalytically active in oxidation, an oxo-diperoxo configuration may be a pre-requisite [41,83,84].

4. Conclusions

A heterogeneous catalyst has been developed for oxidation of organic sulfides by hydrogen peroxide under mild reaction conditions, by immobilizing peroxotungstate on poly(acrylonitrile) matrix. It is remarkable that the catalyst can be effectively used for obtaining high purity sulfoxide as well as sulfone from the corresponding aryl or alkyl sulfide and DBT in excellent yield and high TOF by a versatile variation of reaction conditions.

The significant advantages offered by the developed protocol include (i) control over degree of oxidation of products; (ii) chemoselectivity of the catalyst toward sulfur group of substituted sulfides and sulfoxides with other oxidation prone functional groups; (iii) avoidance of chlorinated solvent or other additives; (iv) easy regeneration and reusability of the catalyst for several catalytic cycles without any change in its activity. Moreover, simplicity in the method of preparation of the catalyst involving easily available starting materials and its non-hygroscopic and stable nature are additional attractive features associated with the catalyst. The findings confirm that immobilization of pW species on the PAN matrix enhances its stability, and leads to an improvement in the overall efficiency of the pW catalyst. It is reasonable to expect that the synthesized catalyst may emerge as a useful addition to the range of ecologically suitable oxidation catalysts with the potential for accomplishing some of the goals of green chemistry. The work on other applications of **PANW** is now underway in our laboratory.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.12.025.

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