Macromolecular metal complexes of Nb^V as recoverable catalysts for selective and eco-compatible oxidation of organic sulfides in water

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The activity of a pair of peroxoniobium(V) species immobilized on water soluble non-crosslinked polymers (WSP) formulated as, [Nb(O$_2$)$_3$(sulfonate)$_2$]-PSS [PSS = poly(sodium styrene sulfonate)] (catalyst **1**) and [Nb$_2$(O$_2$)$_6$(carboxylate)$_2$]-PA [PA = poly(sodium acrylate)] (catalyst **2**) as efficient and recyclable catalysts for selective sulfoxidation of a variety of organic thioethers with 30% H$_2$O$_2$ in water, is described. A new polymer anchored macrocomplex (catalyst **1**) has been synthesized from the reaction of sodium tetraperoxoniobate (**NaNb**) with 30% H$_2$O$_2$ and the macromolecular ligand poly(sodium styrene sulfonate) in an aqueous medium. The catalyst has been comprehensively characterized by spectral and other physicochemical techniques. Apart from being high-yielding and operationally simple, the additional important features which enhance the sustainability of the high yielding water-based oxidation protocol include chemoselectivity of the oxidation for sulfides and easy recyclability of the catalyst with consistent activity and selectivity for several cycles of oxidation.

Keywords: Aqueous phase reaction, peroxoniobium(V) catalyst, water soluble polymers, chemoselective sulfoxidation, non-polluting oxidation catalyst.

Introduction

As sustainability of a chemical transformation is mainly governed by the solvents, apart from the reagents and catalysts used, water-centred organic synthesis is currently receiving tremendous importance mainly owing to the increasing acceptance of water as the ultimate green solvent[1,2]. Being a natural solvent, water is inexpensive, abundant, non-toxic with inherent favourable attributes such as redox stability, high heat capacity, non-flammability etc., which can often be used as an alternative to traditional organic solvents[2–10]. As has been comprehensively reviewed by Lindstrom[2] recently, progress in water-based organic reactions have triggered a simultaneously growing demand for water-tolerant catalysts and water soluble ligands to support aqueous phase organic reactions.

The application of soluble polymers to recover catalyst in synthetic approaches related to peptide synthesis was introduced by Merrifield decades back[11–13] paving the way toward developing immobilized homogeneous catalysts[14,15]. However, the concept of application of linear water soluble polymers as support for immobilizing active metal complexes in catalyst design appears to be still new and relatively unexplored. Water soluble macromolecular metal complexes find extensive utility in diverse fields including pharmaceuticals[16–18] and environmental applications[19–21].

Significantly, very recently we have introduced for the first time a set of peroxomolybdenum(VI) species immobilized on linear water soluble polymers as versatile and recyclable catalysts for selective oxidation of organic sulfides to sulfoxide in water with 30% H$_2$O$_2$[22]. Furthermore, in the recent past, we have developed several new polymer immobilized homogeneous as well as heterogeneous catalysts using peroxo derivatives of metals such as vanadium[22,23], molybdenum[23–26] and tungsten[26,27] which efficiently mediated variety of organic oxidations including phenol hydroxylation, oxidative bromination and sulfide oxidation under environment compatible reaction condition.

Selective oxidation of organic sulfides constitute one of the most fundamentally important class of transformations in the domain of organic chemistry[28–36]. As has been adequately highlighted in the literature[31–36], sulfoxides and sulfones serve as versatile building blocks for gaining access to a variety of chemically and biologically active molecules, including drugs and chiral auxiliaries. A plethora of promising

catalytic strategies for selective sulfoxidation have emerged in the past few years based on transition metal catalysts, particularly those from groups 4-7 in their highest oxidation states[37–49]. Many of the available protocols, however, rely upon the use of toxic and volatile organic solvents and harmful oxidants or require complex catalyst preparation or harsh reaction conditions. Such factors may ultimately compromise eco-sustainability of otherwise efficient oxidation process. There are very limited reports on metal-catalyzed sulfoxidation reaction in an aqueous medium[25,43,45,50–57]. Thus the demand for alternative catalytic oxidation processes that employ benign solvent, green oxidants and reagents which co-produce only innocuous waste appears to continue unabated[27,46–49,58–60].

In view of the aforementioned observations in the present study, we have directed our efforts to develop new water-compatible catalyst to accomplish organic oxidation in aqueous medium, by anchoring peroxo niobium species to water soluble polymer matrices. As our goal has been to generate safer catalysts and methodologies, we considered Nb to be an appropriate choice mainly due to the facts that, Nb has been reported to be non-toxic to animals and catalysis by peroxoniobium (**pNb**) compounds, appears to be a field of growing interest[57,61–69], although the catalytic potential of discreet synthetic heteroligand **pNb** complexes as oxidation catalysts has rarely been explored. The **pNb** species generated *in situ* in the presence of H_2O_2 have been reported to catalyze variety of oxidations including oxidation of alcohol[61–63], epoxidation of alkene[61,62,65,66] and oxidation of sulfides[64,67,68]. It is notable that a set of water soluble peroxoniobium complexes synthesized recently in our laboratory have demonstrated excellent catalytic activity in sulfoxidation of thioethers with H_2O_2 in water, with high selectivity and functional group compatibility[57].

In this article, the preparation and characterization of a new peroxoniobium derivative immobilized on water soluble polymer matrix, $[Nb(O_2)_3(sulfonate)_2]$-PSS [PSS = poly(sodium styrene sulfonate)] is described. The catalytic performance of the newly synthesized catalyst as well as a polyacrylate anchored **pNb** macrocomplex reported previously by us (catalyst **2**), have been evaluated in the selective oxidation of sulfides to obtain sulfoxides with H_2O_2 in an aqueous medium, in terms of selectivity, yield, reusability and sustainability.

Experimental

Materials and methods

The chemicals used were all reagent-grade products. Niobium pentoxide, poly(sodium styrene sulfonate) (M_w = 200,000), poly(sodium acrylate) (M_w = 2100), used in this study were obtained from Sigma-Aldrich Chemical Co., Milwaukee, USA, sodium thiosulfate from Merck, India, hydrogen peroxide (30%) from Rankem, India. $[Nb_2(O_2)_6(carboxylate)_2]$-PA [PA = poly(sodium acrylate)] (catalyst **2**) was prepared according to procedure described in our earlier paper[70]. For catalyst **2**, FT-IR (KBr pellet, cm^{-1}): 1710, 1571 [$v_{asym}(COO)$], 1408 [$v_{sym}(COO)$], 593 [$v_{asym}(Nb-O_2)$], 549 [$v_{sym}(Nb-O_2)$], 813, 826, 846 [$v(O-O)$]; ^{13}C NMR (ppm): 36.04 and 45.75 and ^{93}Nb (ppm): –1530.

Synthesis of [Nb(O$_2$)$_3$(sulfonate)$_2$]-PSS (1)

Sodium tetraperoxoniobate, $Na_3[Nb(O_2)_4]\cdot13H_2O$ (0.68 g, 1.3 mmol) was dissolved in 5 mL (44 mmol) of 30% H_2O_2 and then HNO_3 solution (*ca.* 4 *M*) was added to the above solution dropwise with constant stirring to maintain the pH of the reaction medium to 5.0. Keeping the temperature of the reaction mixture below 4°C in an ice bath, 1 mL of 30% poly(sodium 4-styrene sulfonate) (PSS) was added to it. The pH of the mixture was recorded to be *ca.* 5.0. After 3 h of contact time, solvent induced precipitation was carried out by adding pre-cooled acetone under vigorous stirring. After being allowed to stand for 30 min, the supernatant liquid was decanted off and the residue was repeatedly washed with pre-cooled acetone under scratching. The microcrystalline product was separated by centrifugation and dried *in vacuo* over concentrated sulfuric acid. The metal loading calculated from the observed niobium content is 1.62 mmol g^{-1} of polymer for $[Nb(O_2)_3(sulfonate)_2]$-PSS [Table S1, (Supplementary information)]. FT-IR (KBr pellet, cm^{-1}): 1217, 1181 (S-O), 593 [$v_{asym}(Nb-O_2)$], 549 [$v_{sym}(Nb-O_2)$] and 813, 827, 846 [$v(O-O)$]; Raman (cm^{-1}): 1210, 1148 (S-O), 543 [$v_{asym}(Nb-O_2)$], 471 [$v_{sym}(Nb-O_2)$] and 812, 841, 859 [$v(O-O)$].

General procedure for oxidation of sulfides to sulfoxides (catalyst: 1 or 2)

In a representative procedure, to a solution of a catalyst (0.002 mmol) in water (5 mL) organic substrate (5 mmol) was added maintaining a catalyst:substrate molar ratio of 1:2500. The oxidant, 30% H_2O_2 (1.13 mL, 10 mmol) was

then added to it (substrate:H$_2$O$_2$ ratio of 1:2). The reaction was conducted at 0°C in an ice bath under continuous magnetic stirring. The progress of the reaction was monitored by thin-layer chromatography (TLC) and GC. After completion of the reaction, the products were extracted with diethyl ether and dried over anhydrous Na$_2$SO$_4$ 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, ^{1}H NMR, and ^{13}C NMR spectroscopy, and in the case of solid sulfoxides products, in addition to the above spectral analysis, we have also carried out melting point determination [see Text S1 (Supplementary information)].

Regeneration of the catalyst

The catalyst recyclability experiment was carried out using methyl phenyl sulfide (MPS) as representative substrate employing either of the following procedures. After extraction of the organic reaction product subsequent to completion of the reaction, the aqueous part of the reaction mixture was transferred to a beaker. Keeping the solution in an ice bath, 30% H$_2$O$_2$ was added to it maintaining a Nb:peroxide ratio of 1:2, followed by addition of pre-cooled acetone under constant stirring until a white pasty mass separated out. From this precipitate, the catalyst was finally obtained as a microcrystalline solid by precipitation with acetone. The regenerated **pNb** catalyst was then placed into a fresh reaction mixture consisting of MPS and hydrogen peroxide in water, and the reaction was allowed to proceed under optimized conditions as mentioned above. The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the process was repeated for a total of six reaction cycles.

In an alternative procedure, recycling of the catalyst could be performed *in situ* after completion of the reaction cycle and extraction of the organic reaction product. Regeneration of the used reagent could be achieved by adding 30% H$_2$O$_2$ and a fresh batch of substrates to the aqueous portion of the spent reaction mixture, maintaining the same procedure as mentioned above and conducting the reaction under optimized conditions. Each of the procedures was repeated for six reaction cycles.

Results and discussion

Catalyst preparation and characterization

The white microcrystalline **pNb** catalyst **1**, was obtained by devising a fairly straightforward synthetic methodology involving the reaction of water soluble precursor complex Na$_3$[Nb(O$_2$)$_4$]·13H$_2$O (**NaNb**), used as the source of niobium, with 30% H$_2$O$_2$ and the WSP, poly(sodium 4-styrene sulfonate) (PSS) maintaining the pH of the solution at *ca.* 5. Following a somewhat similar procedure reported recently by our group[70], the polyacrylate anchored **pNb** catalyst **2**, [Nb$_2$(O$_2$)$_6$(carboxylate)$_2$]-PA (**1**) [PA = poly(sodium acrylate)] has been synthesized. The maintenance of required time and temperature at ≤ 4°C was observed to be additional important factor for obtaining the target compounds. The compounds were isolated finally by solvent induced precipitation with acetone, which is an effective and general way of isolating soluble polymers. The catalysts **1** and **2** are stable in solid state for several weeks, when stored dry at < 30°C.

The elemental analysis data for each of the polymeric compounds indicated the presence of three peroxo groups per metal centre for **1**. The niobium loading on the compound, corresponds to 1.62 mmol g^{-1} of the polymeric support, which was calculated on the basis of Nb content, obtained independently from EDX analysis as well as inductively coupled plasma optical emission spectrophotometer (ICP-OES) analysis [Table S1 (Supplementary information)]. In case of catalyst **2**, Nb loading of 2.08 mmol g^{-1} of polyacrylate support, was found previously to be relatively higher[70]. Consistent with the presence of Nb in its +5 oxidation states, the immobilized **pNb** compound was diamagnetic in nature, as was evident from the magnetic susceptibility measurement.

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

The morphological changes taking place on the surface of the polymer after loading of the peroxometallate to the polymer matrix was studied by scanning electron microscopy. The micrograph of the polymer-anchored complex showed significant roughening of its surface, in contrast to the smooth surfaces of the pure polymer (Fig. 1), and revealed that the metal ions are distributed across the surface of the polymer.

Energy dispersive X-ray spectroscopic analysis, which provides *in situ* chemical analysis of the bulk, was carried out focusing multiple regions over the surface of the **1**. EDX spectra clearly showed Nb, Na, C, S and O constituents for
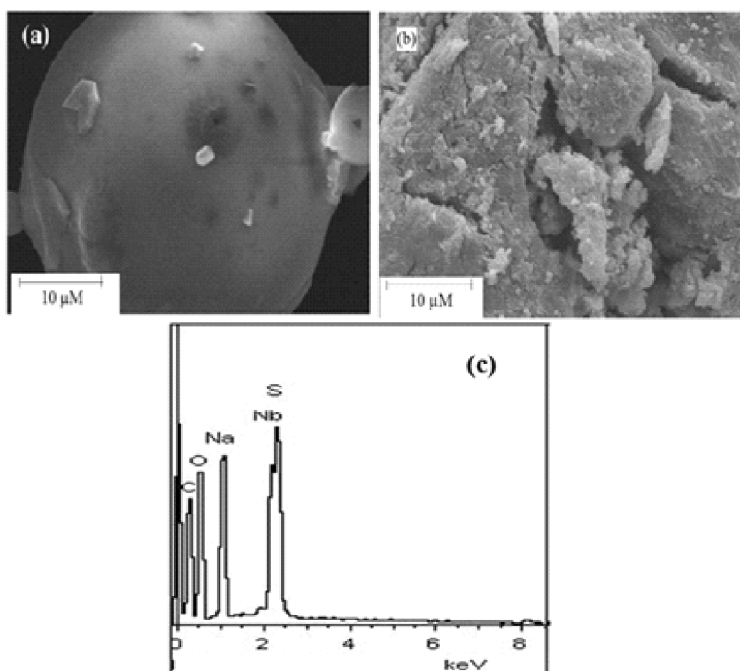
Fig. 1. SEM of (a) PSS, (b) catalyst **1** and (c) EDX of catalyst **1**.

1. The result presented in Table S1 for **1** is the average of the data from these regions. The data obtained from energy dispersive X-ray spectroscopy on the composition of the developed compound resemble those of the elemental analysis values [Table S1 (Supplementary information)].

IR and Raman spectral studies

FTIR and Raman spectra of the catalyst **1**, provided clear indication for successful anchoring of the peroxoniobium species to PSS, by exhibiting the characteristic spectral pattern. In the spectrum of the pure polymer PSS, the bands at 1197 cm^{-1} and 1039 cm^{-1} represent S-O stretching for asymmetric and symmetric absorption bands of SO_2, respectively[71,72]. In the spectrum of the catalyst **1** (Fig. 2), a broad band with distinct absorptions at 1217 and 1181 cm^{-1}, in addition to symmetric vibration of S-O at 1033 cm^{-1}, appeared which may be ascribed to the splitting of S-O stretching vibrations originating from complexed sulfonate group[71,73–75]. The spectrum of the compound exhibited typical absorptions at *ca.* 1637 and 1499 cm^{-1} due to its phenyl group and bending CH_2, respectively[71,73,76].

The IR spectrum of the macro complex **1**, also exhibited three typical peaks at 813, 827 and 846 cm^{-1} attributable to
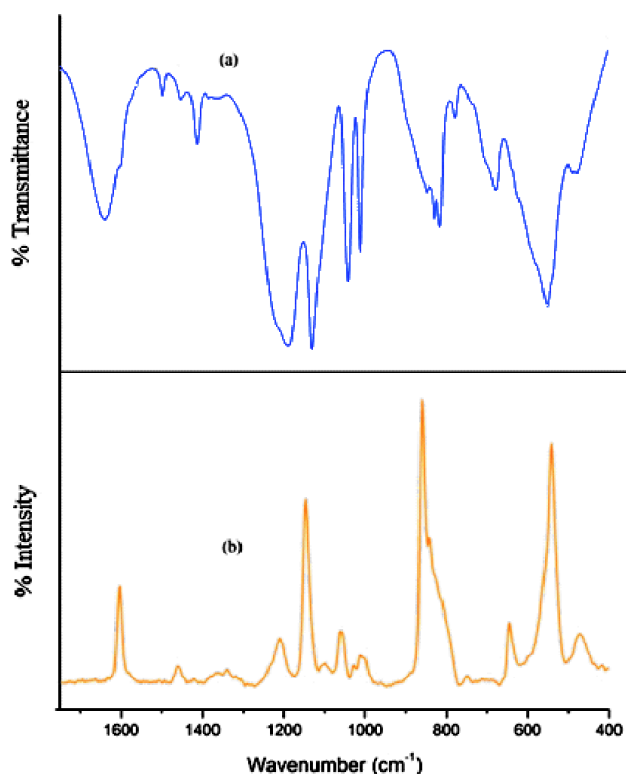

Fig. 2. (a) IR and (b) Raman spectra of **1**.

ν(O-O) mode of triperoxoniobium species[77,78] in addition to the ν_{as}(Nb-O$_2$) and ν_s(Nb-O$_2$) modes at 550 and 489 cm^{-1}, respectively (Fig. 2)[77,78]. Appearance of broad strong absorptions in the vicinity of 3500–3400 cm^{-1} indicated the presence of lattice water in the complex. The IR results were supported by the complementary Raman spectrum (Fig. 2), which showed typical peaks at 812, 841, 859, corresponding to ν(O-O), and at 543 and 471 cm^{-1} due to ν_{asym}(Nb-O$_2$) and ν_{sym}(Nb-O$_2$) vibrations, respectively of the [Nb(O$_2$)$_3$] moiety. Additionally, the spectrum also showed asymmetric band of SO$_2$ at 1148 cm^{-1} as well as symmetric vibration of S-O at 1028 cm^{-1} that can be attributed to complexed sulfonate.

TGA-DTG analysis

The TGA-DTG profile of the poly(styrene sulfonate) bound **pNb** compound (Fig. 3), revealed that the compound undergo gradual decomposition on heating up to a final temperature of 700°C. The first stage of decomposition, with the liberation of lattice water molecules, occurs in the temperature range of 40–105°C (Fig. 3). The subsequent decomposition stage has been observed in the range of 126–222°C, which may be ascribed to the loss of peroxo groups from the com-

plex. The absence of peroxide group in the decomposition product, isolated at this stage, was also verified by its IR spectrum. After the initial dehydration and loss of peroxo groups, a two stage decomposition in the range of 370–613°C, which is possibly due to loss of the sulfonate group and rupturing of polymers occurs. By analogy with the TGA data available for poly(vinyl sulfonate) these decompositions in the range of 370–493°C and 503–613°C, have been ascribed to loss of sulfonate group and rupturing of the polymer accompanied by evolution of ethylene, water, SO$_2$ and CS$_2$[79]. The total weight loss which occurred during the course of the overall decomposition process viz. loss of lattice water, coordinated peroxide and polymeric functional, on heating the compound up to a final temperature of 700°C was recorded to be 36.8%.

The residue remaining from the **pNb** compounds after their complete degradation was characterized to be oxoniobate species. The IR spectra of the residue showed the characteristic ν(Nb=O) absorptions and complete disappearance of the signature peaks pertaining to peroxo as well as polymer support of the original compounds. The TGA-DTG analysis data for the compounds thus furnished further
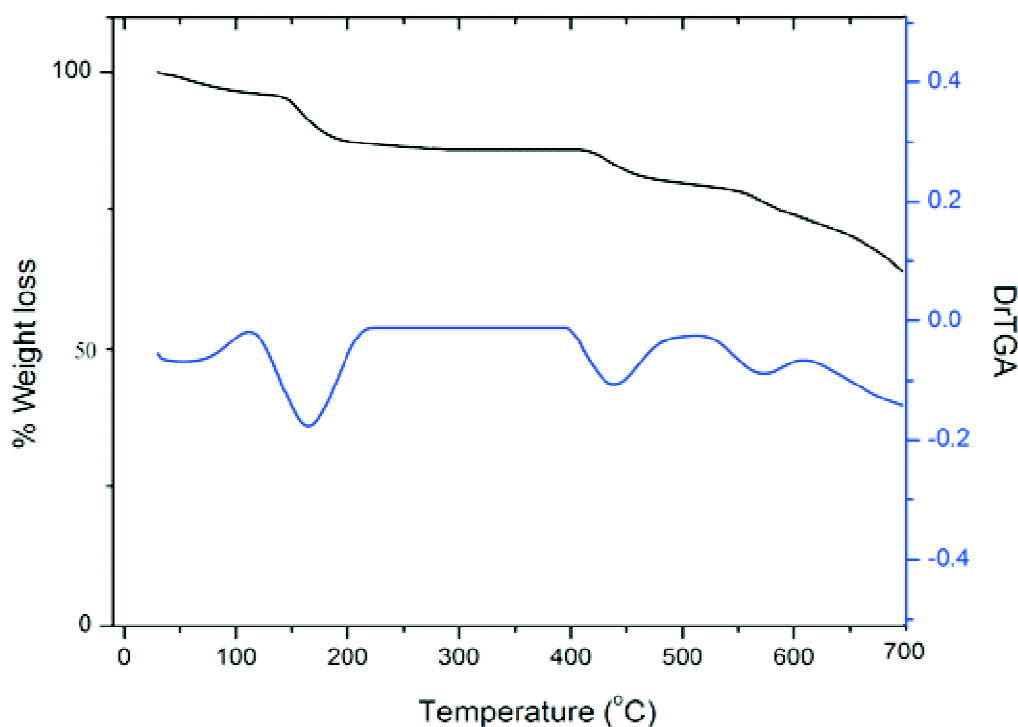

Fig. 3. TGA-DTG plot of **1**.

endorsement in support of the composition and formula assigned to the compounds.

^{13}C and ^{93}Nb NMR studies

In the ^{13}C NMR spectrum of the uncomplexed polymer PSS, the resonances due to chain carbon atoms of CH_2 and CH groups occur at 44.14 ppm and 40.52 ppm, respectively [Table S2 (Supplementary information)]. After metal anchoring, position of these peaks did not undergo any significant shift as observed in the spectrum of catalyst **1**, with the CH_2 and CH resonances appearing at 43.26 ppm and 40.44 ppm, respectively. Thus it is inferred that chain carbon atoms of the polymer support are not greatly affected by metal anchoring via pendant sulfonic acid groups of the polymer chain, as these groups are well separated from the carbon atoms of the polymer chain. We have previously made analogous observations while dealing with other peroxometal compounds anchored to sulfonate containing macro ligands[25].

Thus, ^{93}Nb NMR spectroscopy is a highly useful technique to study the local environment of niobium, as it has been demonstrated that the ^{93}Nb NMR chemical shift is sensitive to the co-ordination number of Nb sites[80]. With 100% natural abundance, ^{93}Nb is one of the most NMR receptive nuclei as it is the only magnetically active isotope of niobium with beneficial NMR properties including the high magnetogyric ratio[81]. In the ^{93}Nb NMR spectrum of macro complex **1,** a single resonance at –1537 ppm (Fig. 4) was observed, which is close to the resonance position of –1530 ppm observed previously in the spectrum of the catalyst **2**, the PA bound **pNb** complex[70]. For the precursor complex, sodium tetraperoxoniobate species, **NaNb**, the peak was observed previously at –1481 ppm[70]. These resonance positions are within the range that corresponds to an eight co-ordinated environment for Nb, which is in agreement with the formula assigned to these compounds. The assignment of the peaks in the present study was on the basis of available literature[80]. Appearance of a single peak in the NMR spectrum of these systems testifies to the existence of Nb^V in a single co-ordination environment in each of them. It is worthy to note that the spectral pattern remained practically unchanged over a period of 12 h. Thus the ^{93}Nb NMR spectrum provided crucial information pertaining to structure and bonding in the **pNb** containing macromolecular complexes, as well as their nature and stability in solution.
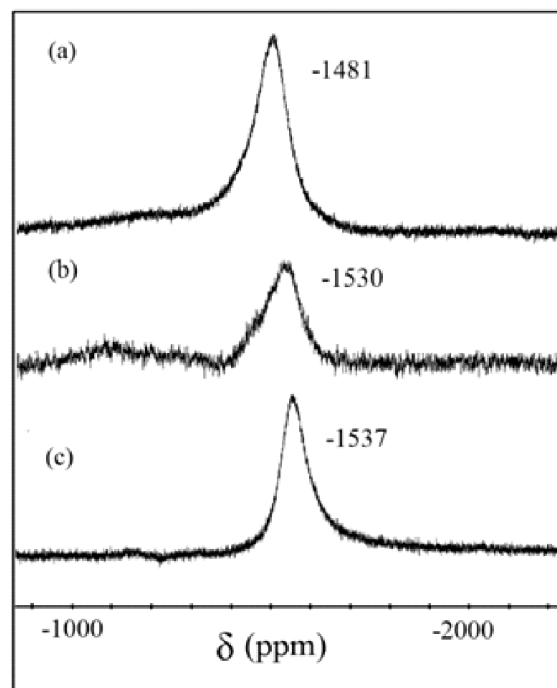

Fig. 4. ^{93}Nb NMR spectra of 0.2 mM solution of (a) **NaNb**[70], (b) **2**[70] and (c) **1** in D_2O.

Based on the above analysis, structure of the type shown in Fig. 5 has been envisaged for the polymer-anchored **pNb** complex, **1**. The proposed structure for the complex **1** includes Nb with unidentate sulfonate group, side-on-bound three peroxo moieties as shown in Fig. 5.

Catalytic activity of compounds 1 and 2

Oxidation of sulfides to sulfoxides

In order to assess the performance of the immobilized **pNb** complexes **1** and **2** as catalysts in oxidation of organic thioethers, a preliminary experiment was carried out using MPS as model substrate and 30% aqueous H_2O_2 as a terminal oxidant (1 equiv.) in the presence of the water-soluble catalyst **1**. The reaction was conducted in water at ambient temperature under magnetic stirring, maintaining a catalyst:substrate molar ratio of 1:1000. The reaction under these conditions afforded a mixture of sulfoxide and sulfone, as presented in Table 1 (entry 1). As the reaction was observed to be mildly exothermic, we have attempted to control the degree of oxidation by lowering the reaction temperature to 0°C by conducting the reaction in an ice bath. As has been anticipated, under these conditions total conver-
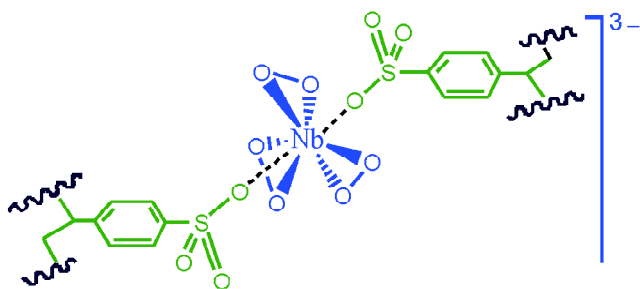
Fig. 5. Proposed structure of **pNb** catalyst **1** ("⌇⌇⌇⌇" represents polymer chain).

sion of MPS to pure sulfoxide could be attained with excellent TOF by increasing the oxidant:substrate molar ratio as 2:1 without altering the other reaction conditions. Subsequently, the reaction conditions for selective sulfoxidation including substrate:oxidant stoichiometry, catalyst concentration, solvent type and reaction temperature were optimized.

Next, we have investigated the influence of the catalyst concentration on the rate and selectivity of the reaction. As shown in Table 1, increase in catalyst amount resulted in a lowering of the corresponding TOF value, although the reaction time was reduced considerably. Interestingly, a reason-ably good TOF could be attained even at a catalyst:substrate ratio of 1:3000 (Table 1, entry 7). The optimal catalyst:substrate ratio for achieving the highest TOF along with complete selectivity was however, found to be 1:2500. A control experiment conducted in absence of the catalyst was observed to be slow and non-selective which provided a mixture of sulfoxide and sulfone in < 9% yield under the standard reaction conditions (Table 1, entry 11)[57]. Thus it is evident that the **pNb** catalyst plays a crucial role in accelerating the oxidation reactions. We have also compared the catalytic efficiency of the supported **pNb** catalyst with that of neat tetraperoxoniobate (**NaNb**) complex Na$_3$[Nb(O$_2$)$_4$]·13H$_2$O under the optimized condition which revealed that the reaction was non-selective[57]. Although a reasonably good TOF was obtained in presence of **NaNb** (Table 1, entry 10), the reaction proceeded with loss of selectivity. From these observations, it is apparent that the superior activity and sulfoxide selectivity displayed by the catalyst **1** is a consequence of immobilization of the **pNb** species on the WSP support.

The effect of solvent on the sulfoxidation reaction was examined using relatively safer organic solvents such as CH$_3$OH and CH$_3$CN in the oxidation of MPS, strategically

Table 1. Optimization of reaction conditions for selective oxidation of methyl phenyl sulfide (MPS) by 30% H$_2$O$_2$ catalyzed by **pNb** complexes^a

Entry	Molar ratio Cat:MPS	30% H$_2$O$_2$ (equiv.)	Solvent	Time (min)	Isolated yield (%)	**1a:1b**	TON	TOF (h^{-1})
1	1:1000^b	1	H$_2$O	80	70	75:25	700	526
2	1:1000^c	1	H$_2$O	80	60	100:0	600	451
3	1:1000^c	2	H$_2$O	45	95	100:0	950	126-7
4	1:500^c	2	H$_2$O	35	96	80:20	480	827
5	1:2000^c	2	H$_2$O	52	94	100:0	1880	2161
6	1:2500^c	2	H$_2$O	55	96	100:0	2400	2609
7	1:3000^c	2	H$_2$O	80	94	100:0	2814	2116
8	1:2500^b	2	CH$_3$OH	125	80	100:0	2000	962
9	1:2500^b	2	CH$_3$CN	130	75	100:0	1875	864
10^d	1:2500^b	2	H$_2$O	95	97	55:45	2425	1531
11^e	-	2	H$_2$O	50	9	90:10	-	-

^{a}Reactions were carried out with 5 mmol of substrate in 5 mL of solvent. Catalyst amount = 3.09 mg for 0.005 mmol of Nb (catalyst **1**). ^{b}Reaction at room temperature. ^{c}Reaction at 0 ^{o}C in ice bath. ^{d}Na$_3$[Nb(O$_2$)$_4$]·13H$_2$O as catalyst[57]. ^{e}Blank experiment (without catalyst)[57].

precluding the use of hazardous chlorinated solvents. Significantly, in addition to water, the methodology was observed to be compatible with these polar organic solvents as well. However, to our pleasure, water emerged to be the best solvent providing highest TOF along with product selectivity notwithstanding the poor solubility of the catalysts in neat organic solvents. The catalytic process however, attains homogeneity as each of the catalysts dissolves completely in these water-miscible solvents in the presence of aqueous H_2O_2. It is notable that, the sulfoxidation reaction in the chosen organic solvents occurred at room temperature, unlike in case of water-based reaction where an ice-bath temperature was required to be maintained. MeOH proved to be a relatively better solvent, compared to acetonitrile, affording both product selectivity and high yield at ambient temperature (Table 1, entry 8). Our results are in agreement with earlier findings showing chemoselective sulfoxidation being favoured in polar protic solvent with strong hydrogen bonding ability[27,45,57,82–84]. Importantly, the sulfoxidation reaction has been carried out at the natural pH attained by the reaction mixture (*ca.* 5). Since our goal has been to maintain a mild reaction condition, addition of acid or other additives was avoided as far as possible.

Subsequent to standardization of the reaction condition for selective sulfoxidation of the model substrate in water, we explored the wider applicability of the protocol using a

Table 2. Selective oxidation of sulfides to sulfoxides catalyzed by catalysts **1** and **2**[a]

$$\text{R-S-R'} \xrightarrow[\text{30\% } H_2O_2 \text{ (2 equivalents), 0 °C, } H_2O]{\textbf{1 or 2, (C:S = 1:2500)}} \text{R-S(=O)-R'}$$

Entry	Substrate	1				2			
		Time (min)	Isolated yield (%)	TON[b]	TOF[c] (h⁻¹)	Time (min)	Isolated yield (%)	TON[b]	TOF[c] (h⁻¹)
1.	(phenyl-S-ethyl)	55	96	2400	2609	60	94	2350	2350
		55	93[d]	2325	2527	60	92[d]	2300	2300
		55	94[e]	2350	2554	60	93[d]	2325	2325
2.	(tolyl-S-ethyl)	50	95	2375	3167	55	93	2325	2527
3.	(phenyl-S-allyl)	90	92	2300	1533	100	93	2325	1392
4.	(phenyl-S-vinyl)	300	93	2325	465	315	94	2350	447
5.	(phenyl-S-ethanol)	90	97	2425	1617	100	96	2400	1437
6.	(diphenyl sulfide)	330	92	2300	418	360	91	2275	379
7.	(diethyl sulfide)	15	97	2425	9700	15	96	2400	9600

[a]Optimized condition: 5 mmol substrate, 10 mmol 30% H_2O_2 and 0.002 mmol catalyst in H_2O at 0°C. [b]TON (turnover number) = mmol of product per mmol of catalyst. [c]TOF (turnover frequency) = mmol of product per mmol of catalyst per hour. [d]Yield of 6th reaction cycle. [e]Scale up data (6.24 g of MPS).

variety of aryl alkyl, aryl vinyl, aryl alcohol and dialkyl sulfides. Our results presented in Table 2 confirm that both the catalysts were effective in leading to the facile and selective transformation of each of the substrates to the corresponding sulfoxide with impressive yield, although catalyst **1** exhibited higher performance in comparison to catalyst **2** (Table 2). The nature of the substrate and the attached substituent, appeared to influence the rates of oxidation[60,85], although the protocol worked well for both aliphatic and aromatic substrates irrespective of having electron-donating or electron withdrawing moieties. It is noteworthy that even in the case of a less nucleophilic diaromatic sulfide, the corresponding sulfoxide was effectively obtained. It has been known that the rate of oxidation of sulfide with H_2O_2 increases[60,85] with its increasing nucleophilicity. Our observations that dialkyl sulfides were oxidized by H_2O_2 at a faster rate leading to the highest TOF, relative to conjugated systems such as allylic and vinylic sulfides or aromatic sulfides, are thus consistent with the previous findings[23–25,27,57].

An important feature of the developed catalytic protocol, is the chemoselectivity of the catalysts for the sulfur group of substituted sulfides with co-existing sensitive functional groups (Table 2, entries 3–5). The benzylic and alcoholic sulfides could be oxidized to the corresponding sulfoxide without affecting the benzylic C-H bond or the -OH group of alcoholic sulfides. Similarly, allylic and vinylic sulfoxides were obtained without an epoxidation product.

Recyclability of the catalysts

The recyclability of the polymeric catalysts for subsequent cycles of oxidation was examined under optimized reaction condition employing MPS as the substrate. One of the advantages often offered by the use of a water soluble catalyst in aqueous medium, is the possibility of quantitative recovery of the catalyst through simple phase separation due to poor solubility of the organic reaction products in water. In the present case, the catalysts could be regenerated by treating the aqueous extract of the spent reaction mixture, after separation of the organic reaction products, with 30% H_2O_2 and then recovering it by solvent-induced precipitation with acetone. Significantly, regeneration was also very conveniently accomplished *in situ* by charging the aqueous part of the spent reaction mixture with 30% H_2O_2 before adding a

fresh batch of substrates, on completion of each catalytic cycle. The *in situ* approach is undoubtedly more advantageous as the tedious separation and purification steps usually associated with soluble catalysts[4] could be avoided, apart from minimizing the use of organic solvents which are usually associated with soluble catalysts. To our satisfaction, activity and selectivity of the catalysts showed no significant change for at least up to 6 reaction cycles as illustrated in Table 2 (entry 1d) and Fig. 6. The highest overall TOF of *ca.* 17,136 h^{-1} was observed for **1** (*ca.* 14,100 h^{-1} for **2**) after 6 cycles of oxidation of MPS to sulfoxides. Taking into account the mild reaction conditions under which the reactions have been performed, the TOF values obtained appear to be indeed significant.
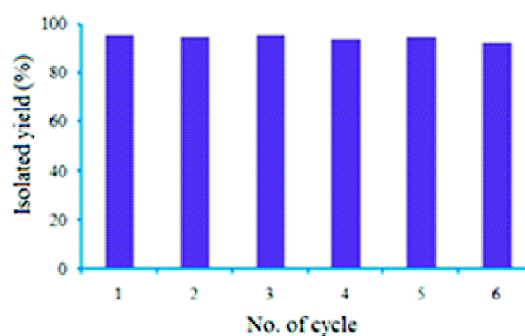

Fig. 6. Catalyst regeneration upto 6th reaction cycle. Recyclability of **1** (used as representative catalyst for macro **pNb** complex) for the selective oxidation of MPS to sulfoxide.

The proposed catalytic cycle

We propose a plausible catalytic cycle based on our present observations and taking into account our previous findings[24,25,27,57] as well as literature available on the catalytic activity of some other peroxoniobium systems[63,77,86]. The scheme of reactions is outlined in Fig. 7 with the catalyst **1** as a representative. As the electrophilicity of metal bound peroxide is known to be considerably higher than H_2O_2, it is expected that in the first step (reaction a), transfer of electrophilic oxygen from triperoxoniobium complex I to the substrate V would occur to yield sulfoxides. In the subsequent step (reaction b), the diperoxoniobate intermediate II would combine with the peroxide of H_2O_2 to regenerate the original triperoxoniobate catalyst to complete a catalytic cycle.
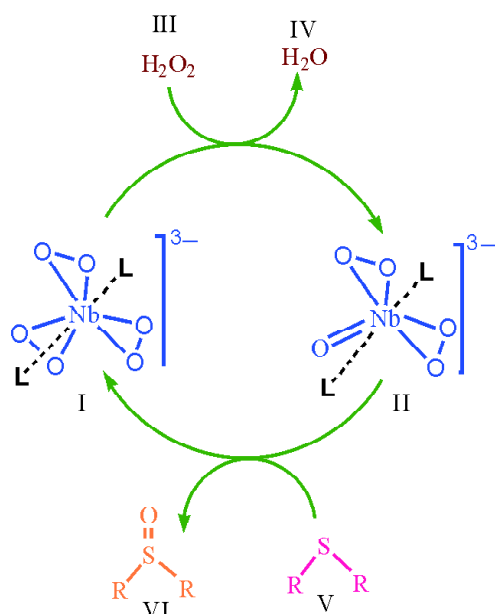
Fig. 7. The proposed mechanism [L = poly(sodium styrene sulfonate)].

Conclusions

We have developed a novel catalyst system based on peroxoniobium derivative immobilized on linear soluble polymers, that are highly effective in mediating clean conversion of sulfides to high purity sulfoxide by H_2O_2, with impressive yield and TOF in aqueous medium. Simplicity in the method of synthesis of the catalysts using a non-toxic metal and water soluble macroligands as support, their recyclability for several catalytic cycles and excellent chemoselectivity toward sulfur group, are some of the environmentally significant characteristics of the catalysts. Sustainability of the protocol is further evident from the fact that the oxidations have been achieved using green oxidant H_2O_2 in neat water, without involving any acid, organic co-solvent or co-catalyst.

Acknowledgements

Supporting information

Analytical data for the polymer-bound peroxoniobate compound **1**, ^{13}C NMR spectral data for catalyst **1**, characterization of sulfoxides.

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