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A water soluble heteropolyoxotungstate as a selective, efficient and environment friendly oxidation catalyst

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Abstract. A series of water soluble Keggin type heteropolyoxotungstates have been tested as oxidation catalysts in aqueous-biphasic media with dilute H_2O_2 (30%) as the oxygen atom donor, without using any phase transfer agent. The Zn substituted polyoxoanion $\{(NH_4)_7Zn_{0.5}[\alpha\text{-}ZnO_4W_{11}O_{30}ZnO_5(OH_2)]\cdot nH_2O\}$ has been found to be the most efficient catalyst, which oxidizes a wide range of organic functionalities with good turnovers and high selectivities. The functionalities that undergo oxidations are: organic sulfides, pyridines, anilines, benzyl alcohols and benzyl halides. The oxidations of sulfides to sulfoxides and/or sulfones have been studied in detail, and a simple kinetic model consisting of two consecutive reactions, is shown to give good fit with the experimental data. In the catalytic system described here product isolation is easy, and the aqueous catalyst solution can be re-used several times with little loss in its efficiency.

Keywords. Heteropolyoxotungstate; oxidation; hydrogen peroxide; pyridine; sulfide; aqueous-biphasic.

1. Introduction

From the point of view of environmentally benign and clean technologies, synthetic strategies that avoid the use of any organic solvents are attractive. Aqueous biphasic catalysis is one such approach.[1–7] Here the reaction medium consists of an aqueous phase that contains a water-soluble catalyst, and a water immiscible organic phase of the neat substrate. For oxidation reactions, the aqueous biphasic oxidation of organic substrates with dilute (30%) aqueous hydrogen peroxide is particularly appealing since dilute hydrogen peroxide is cheap, environmentally clean, and easy to handle.[8]

During the past few years, there have been many reports on the use of Group VI metal complexes as oxidation catalysts and hydrogen peroxide as the oxygen atom donor.[9–12] Polyoxometalates in particular have been used as catalysts to oxidize a broad range of organic substrates.[13–20] As catalyst recovery is an important consideration for any practical catalytic process, many different methodologies have been used for this purpose, e.g. immobilization of the catalyst onto a solid support,[21–25] inclusion of the catalyst in a solvent anchored supported liquid phase,[26–28] and the use of a biphasic (aqueous–nonaqueous) liquid medium with or without a phase transfer catalyst.[29–31] Of these, for reasons already mentioned, the last method is especially attractive. This of course assumes that the catalytic performance i.e. turnovers, selectivity and recyclibility are at an acceptable level.

Detailed studies on the use of sandwich type polyoxometalates as catalysts for the oxidation of a variety of organic functionalities with hydrogen peroxide in aqueous biphasic systems have recently been reported.[32–34] Influenced by this work we decided to study the synthetic and recycle potential of simple Keggin type polyoxometallates as catalysts. We were especially interested in the selective oxidations of pyridine derivatives and organic sulfides. Pyridine N-oxide and heterocyclic N-oxides are useful for their biological activities and as protecting groups, auxiliary agents, and oxidants.[35–37] Oxidations of organic sulfides to sulfoxides and sulfones are also equally important due to the utility of both

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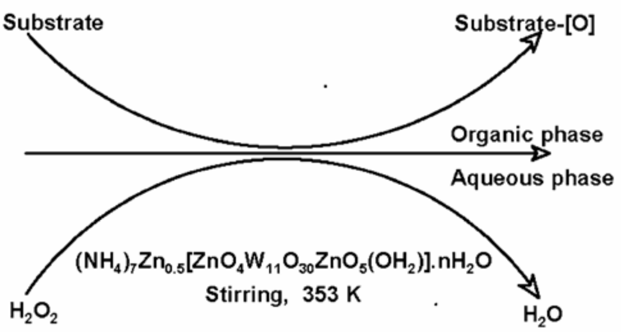
the oxidized products in organic synthesis and pharmaceutical industry.[38–40] However, the *selective* oxidation of sulfides to *sulfoxides* with aqueous hydrogen peroxide is difficult to achieve.[41] In the earlier work where aqueous hydrogen peroxide has been used as the oxidant, sulfones rather than sulfoxides have been found to be the main product.[42,43] Given the synthetic and industrial importance of sulfoxides, aqueous hydrogen peroxide based efficient oxidation of sulfides is therefore an important research target.

Thus, here we report the efficient oxidations of pyridine derivatives and organic sulfides with hydrogen peroxide where $(NH_4)_7Zn_{0\cdot5}[\alpha\text{-}ZnO_4W_{11}O_{30}ZnO_5(OH_2)]\cdot nH_2O$, **1**, is used as the catalyst (scheme 1). We present a simple kinetic model for the oxidation of sulfide that matches well with the experimentally observed data. Such a model is useful as it allows the approximate prediction of batch time for obtaining the best yield under a given set of conditions. Furthermore, we find that the aqueous catalyst solution can be recycled several times with very little loss in the total amount of the heavy metal, which makes the overall process green and practical.

2. Experimental

2.1 *Materials and methods*

All organic sulfides, pyridine derivatives, pyrazine, quinoline, isoquinoline, benzyl halides, benzyl alcohols, anilines, sodium tungstate and zinc nitrate were obtained from Sigma-Aldrich, Germany and were used as received. Distilled water was used throughout all catalytic experiments and for the preparation of the polyoxotungstate. Ethyl acetate, sodium acetate, ammonium acetate and acetic acid were purchased from SD Fine Chemicals, India and were used as received. Proton NMR spectra were taken on a 300 MHz Varian FT–NMR spectrophotometer. Mass spectra were taken on a Micromass Q-TOF mass spectrometer. Gas-chromatographic analyses were carried out using a Shimadzu GC-14A gas chromatograph with FID detector and a capillary column. ^{183}W NMR spectra of **1** was taken on a 500 MHz Varian FT–NMR spectrometer in D_2O as the solvent and 1 M Na_2WO_4 as the reference standard. Thermo Nicolet 320 FT–IR and Perkin Elmer Lambda 950 UV-Vis-NIR spectrophotometers were used for recording IR and electronic spectra, respectively. The bulk tungsten content of fresh and used catalyst **1** was determined on an 8440 Plasma Lab ICP-AES instrument.



Scheme 1. Generalized picture for the aqueous-biphasic oxidation of various organic functionalities by catalyst (**1**) with aqueous hydrogen peroxide as an oxidant.

2.2 *Preparation of catalyst*

The polyoxotungstates $(NH_4)_7Zn_{0\cdot5}[\alpha\text{-}ZnO_4W_{11}O_{30}ZnO_5(OH_2)]\cdot nH_2O$ (**1**) ($n \approx 18$) and the analogous other polyoxotungstates, **2**, **3** and **4** were prepared according to the literature reported procedure.[44] The materials were recrystallized prior to their use as catalysts.

2.3 *General procedures for the catalytic reaction and product characterization*

In a typical experiment 4 μmol (13 mg) of **1** was dissolved in 5 mL of distilled water and 1 mmol substrate was added to it in a 15 mL two necked round bottom flask and it was placed on a magnetic stirrer attached with temperature controller and water condenser under nitrogen atmosphere. The temperature was maintained at 353 K and 4 mmol of 30% (W/V) aqueous hydrogen peroxide (0·41 mL) was added drop-wise into the reaction mixture, which was vigorously stirred. After a suitable time interval the reaction was stopped and the product was separated either by filtration (for solid product) or through solvent extraction with ethyl acetate (for liquid product). The products were analysed by GC, and/or NMR and mass spectrometry.

2.4 *Kinetic modelling*

The differential equations were integrated using ODE solver (ODE23) available in MATLAB 7.0

(The Math Works Inc., USA) with appropriate initial conditions for the variables. The parameters in the model were estimated by fitting the model predictions with the experimental data. ODE23 is a low order method and solves non-stiff differential equations. Sum of square of errors (SSE) was chosen as the objective function to serve as criteria to judge the predictive capability of the model, which was minimized. The minimization was performed using Newton's gradient method available in MATLAB (fmincon). The SSE is the sum of the square of the difference between the model predictions with the actual experimental values. fmincon attempts to find a constrained minimum of a scalar function of several variables starting at an initial estimate. This is generally referred to as constrained nonlinear optimization.

3. Results and discussion

Among the sandwich type polyoxometallates, the Zn^{2+} ion incorporated derivative was reported to be the most active catalyst.[32–34] In contrast, complex **1** belongs to the class of easily synthesized and well characterized mixed metal polyoxo complexes, where the main structural fragment is $[ZnO_4W_{11}O_{30}ZnO_5(OH_2)]^{n-}$ (Keggin-type, α-isomer).[44] One of the 12 octahedrally coordinated tungsten atoms is substituted by one of the Zn^{2+} cation and the corresponding terminal oxygen atom is replaced by an H_2O ligand. The zinc ions are distributed over three different positions: the central (tetrahedral) position, the peripheral (octahedral) positions of the Keggin anion and cationic position outside the polyoxotungstate framework. The ^{183}W-NMR spectrum of **1** in D_2O shows three magnetically inequivalent environments for the tungsten atoms, figure 1 which probably indicates that the active catalyst **1** in water exists partly in a different stoichiometric form.[44]

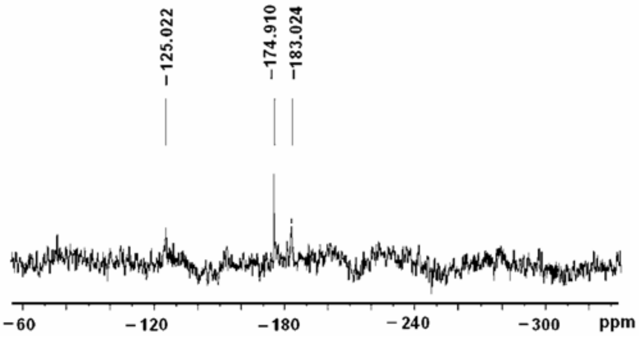
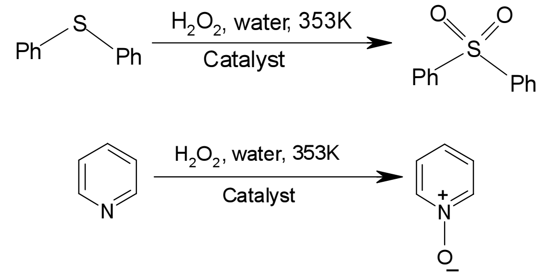


Figure 1. ^{183}W NMR spectrum of **1** in D_2O.

Initially we studied the comparative catalytic performances of **1**, three mixed metal polyoxo analogues of **1**, and Na_2WO_4. The polyoxo analogues of **1** that have been used for this purpose are: $\{(NH_4)_6Ni_{0.5}[\alpha\text{-}MO_4W_{11}O_{30}NiO_5(OH_2)]\cdot nH_2O\}$, (M = Fe, **2**; M = Zn, **3**; M = Co, **4**; $n \approx 18$) made by literature reported procedures.[44] The reactions studied for initial comparative evaluations are the hydrogen peroxide based oxidations of diphenyl sulfide to diphenylsulfone and pyridine to pyridine N-oxide. As can be seen from table 1, for both these reactions **1** is by far the most effective catalyst. This observation is very similar to what has also been reported for the sandwich type complexes.[32,33]

These results prompted us to explore the scope of **1** as the catalyst for a much wider range of sulfides and N-heterocycles. As can be seen from table 2, different types of sulfides and N-heterocycles undergo facile oxidation when **1** is used as the catalyst. In the oxidations of N-heterocycles (table 2, entry 7–12) the yield and product selectivity in every case is close to 100%. In case of pyrazine (table 2, entry 10) mono oxygenated pyrazine is the exclusive product. Presumably, after mono oxygenation due to the strong electronegativity of the oxygen atom the basisity of second N-atom is significantly reduced,

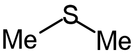
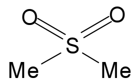
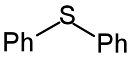
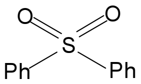
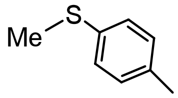
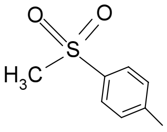
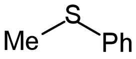
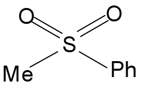
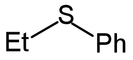
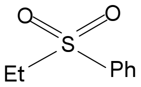
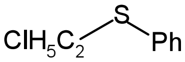
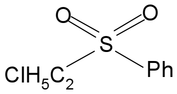
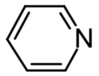
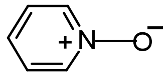
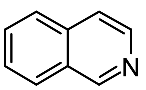
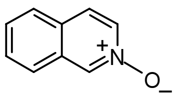
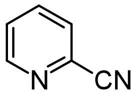
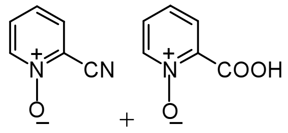
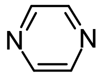
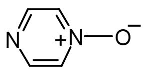
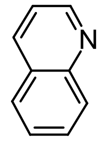
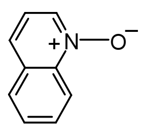
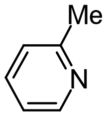
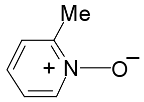
Table 1. Comparative catalytic activity of polyoxometalates, **1**, **2**, **3**, **4** and Na_2WO_4, towards oxidation of diphenylsulfide and pyridine to diphenylsulfone and pyridine N-oxide, respectively.[a]



		Percentage of conversion	
Entry number	Catalyst	Pyridine	Phenyl sulfide
1	**1**	100	100
2	**2**	50	5
3	**3**	65	10
4	**4**	31	2
5	**Na_2WO_4**	0	2

[a] 1 mmol substrate, 4 mmol (30% w/v) H_2O_2, 4 μmol of **1** or **2** or **3** or **4** or Na_2WO_4, 5 mL water, at 353 K, 4 h, with vigorous stirring. Conversions were determined by GC and proton NMR

Table 2. Oxidation of various organic sulfide and pyridine derivatives by **1** in water using hydrogen peroxide as an oxidant.[a]

Entry number	Reactant	Product	% Conversion
1			100
2			100
3			100
4			100
5			100
6			100
7			100
8			100
9			100
10			100
11			100
12			100

[a] 1 mmol substrate, 4 mmol H_2O_2, 4 μmol $\{(NH_4)_7Zn_{0.5}[\alpha\text{-}ZnO_4W_{11}O_{30}ZnO_5(OH_2)]\cdot nH_2O\}$, (**1**), 5 mL water, Time: 4 h, Temperature: 353 K. With vigorous stirring. Products have been characterized by proton NMR, mass spectrometry and/or GC. Conversions were determined by GC and proton NMR

and thus mono-oxygenated pyrazine is the only product. With 2-cyano pyridine a mixture of 2-cyano pyridine N-oxide and 2-carboxylic acid pyridine N-oxide are obtained. This is due to partial hydrolysis of the cyano group in the aqueous H_2O_2 medium.

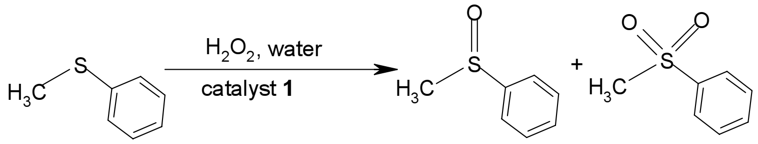
With a substrate to H_2O_2 molar ratio of 1 : 4 and at 80°C, both aromatic and aliphatic sulfides are oxidized to sulfones. In all the cases sulfones are the exclusive products with 100% yield (table 2, entry 1–6). However, as mentioned earlier, one of the primary objectives of the work reported here was to establish reaction conditions that allow maximization of the selectivity towards both sulfoxides and sulfones. Using anisole as the test substrate, several control experiments at different temperatures and substrate to H_2O_2 molar ratios were carried out (table 3). By lowering the temperature and optimizing the substrate to hydrogen peroxide ratio, it is possible to have high selectivity towards sulfoxide with good to acceptable levels of conversion.

Thus, by carrying out the oxidations at 5°C, the sulfoxide yield could be maximized for six representative sulfides (table 4). With lowering of temperature and the substarte : H_2O_2 molar ratio, the conversion decreases but even 55%, the minimum conversion, corresponds to a healthy turnover number of 137. Under the set of conditions used by us, Ph_2S and Et(Ph)S give maximum and minimum selectivity 98 and 87%, respectively, with corresponding conversions (turnovers) of 55% (137) and 70% (175). The observed relationship between relatively low conversion and high sulfoxide selectivity indicates that the oxidation of sulfide to sulfoxide is probably followed by further oxidation of the latter to sulfone, i.e. (1).

$$RSR' \xrightarrow{k_1} RSOR' \xrightarrow{k_2} RSO_2R'. \tag{1}$$

The time monitored concentration profiles of thioanisole and its corresponding sulfoxide and sulfone provide direct evidence for such a conjecture. As shown in figure 2, the concentration profiles of the starting sulfide and its two oxidation products have the characteristic features of consecutive reactions. Furthermore, based on the simple two rate constant model of (1), reasonably good agreement could be obtained between the experimental data points and the predicted concentration profiles. By using time monitored conversion data at four different temperatures, and the two rate constant model, the activation energies associated with k_1 and k_2 could also be

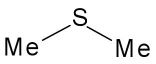
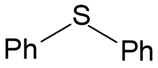
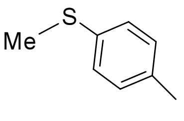
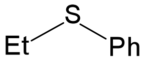
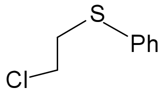
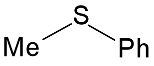
Table 3. Selectivity of oxidation of thioanisole to corresponding sulfoxide and sulfone catalysed by **1** under variation of temperature and H_2O_2 concentration.[a]



Entry number	Temperature	H_2O_2: Substrate	Percentage conversion	Selectivity (sulfoxide)	Selectivity (sulfone)
1	353 K	2	94	15	85
2	353 K	1	69	29	71
3	353 K	4	100	0	100
4	323 K	1	61	67	33
5	300 K	1	31	74	26
6	280 K	1	20	93	7
7	280 K	2	75	91	9

[a]Reaction Conditions: 1 mmol substrate, 4 μmol $[NH_4)_7Zn_{0.5}[\alpha\text{-}ZnO_4W_{11}O_{30}ZnO_5(OH_2)]\cdot nH_2O$, 5 mL water, with vigorous stirring. Conversions were determined by GC

Table 4. Selective oxidation of organic sulfides by catalyst **1** in water using aqueous hydrogen peroxide as an oxidant.[a]

Entry number	Substrate	% Conversion	Selectivity (%) Sulfoxide	Selectivity (%) Sulfone
1		85	90	10
2		55	98	2
3		80	88	12
4		70	87	13
5		76	94	6
6		75	91	9

[a]Reaction conditions: 1 mmol substrate, 2 mmol H_2O_2, 4 μmol $\{(NH_4)_7Zn_{0.5}[\alpha\text{-}ZnO_4W_{11}O_{30}ZnO_5(OH_2)]\cdot nH_2O\}$, (**1**), 5 mL water, Time: 2 h, Temperature: 278 K, with vigorous stirring. Conversions were determined by GC and proton NMR

estimated. As shown in figure 3, the Arrhenius plots show good linearity, and $\Delta E^{\#}$ associated with k_1 and k_2 of thioanisole are found to be 13·9 and 7·2 Kcal, respectively.

As mentioned earlier, oxidations of a few representative benzyl halide, benzyl alcohol and anilines have also been studied to establish the wide scope of the aqueous biphasic catalytic system. Selective

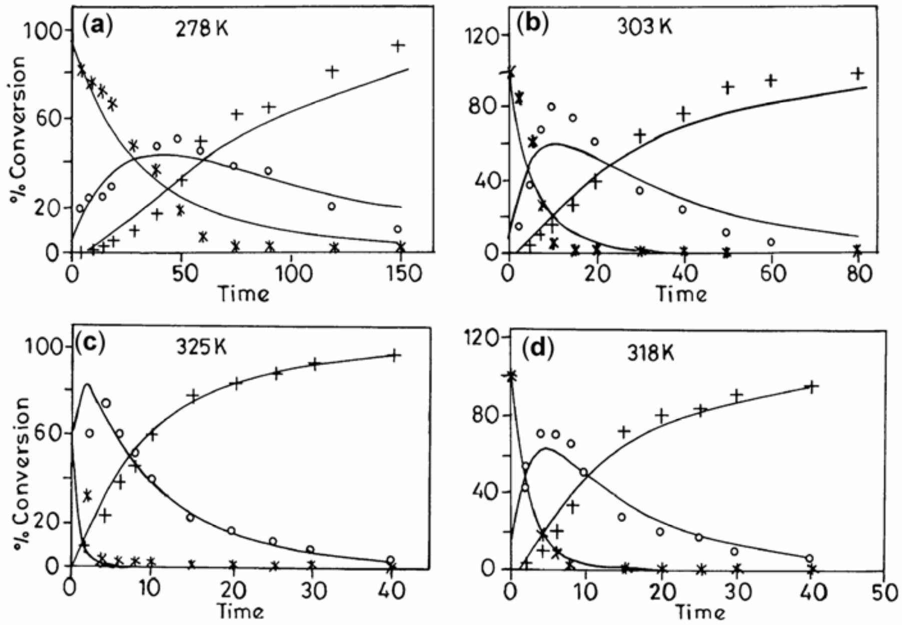


Figure 2. Time monitored conversion plots for the conversion of thioanisole to corresponding sulfoxide and sulfone at four different temperatures. (**a**) at 278 K, (**b**) at 303 K, (**c**) 325 K, (**d**) at 318 K. Experimental concentrations of thioanisole (*), phenylmethylsulfoxide (o), and phenylmethylsulfone (+). The solid lines are the predicted concentration profiles based on the consecutive reactions model. Substrate = 1 mmol; Catalyst = 4 μmol; H_2O_2 = 4 mmol; Water (Solvent) = 5 mL; with vigorous stirring. Products were characterized by GC.

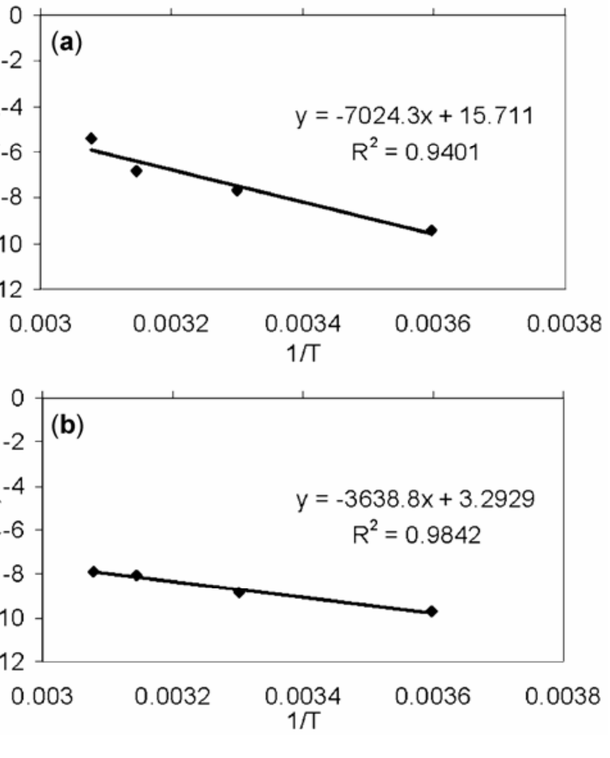
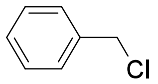
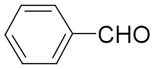
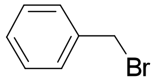
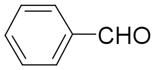
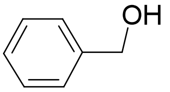
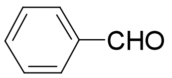
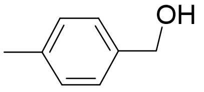
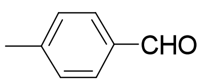
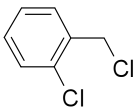
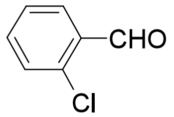
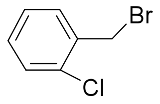
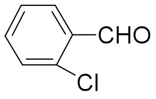
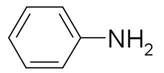
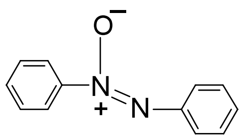
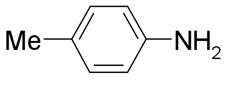
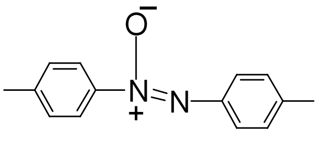
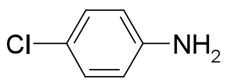
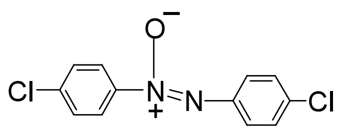
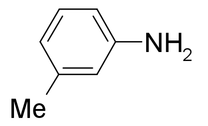
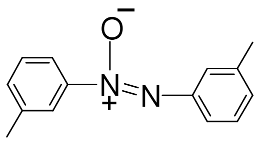


Figure 3. Activation energy plots (Ln *k* vs 1/*T*) (**a**) Ln (k_1) vs 1/*T* and (**b**) Ln (k_2) vs 1/*T*.

oxidations of benzyl halides and alcohols to the corresponding aldehydes are significant reactions, because these aldehydes are used widely.[45,46] As shown in table 5, four benzyl halides and two benzyl alcohols give benzaldehyde or its halo derivatives as the selective products, and only minor ($\leq 5\%$) amounts of benzoic acids are formed. The conversions for all the six substrates are $\geq 74\%$. It may be noted that the oxidations of benzyl halides and alcohols by H_2O_2 in water, using Na_2WO_4 and a phase transfer catalyst has been reported by Noyori and co-workers.[29,30] In contrast to this report, no phase transfer co-catalyst is required in the system described here.

The oxidations of aniline and its derivatives by H_2O_2, using a sandwich type polyoxotungstate as the catalyst are also reported reactions.[32,33] With a few representative substrates, the efficacy of **1** as a catalyst in these reactions has also been studied for completeness. As can be seen from table 5 (entries 7–10), aniline and its derivatives are oxidized to the corresponding dimeric azoxy compounds with high ($\geq 92\%$) conversion and full selectivity.

Table 5. Oxidation of various benzyl halides, benzyl alcohols and aniline derivatives by **1** in water with aqueous hydrogen peroxide as an oxidant.[a]

Entry number	Reactant	Product	% Conversion
1			74
2			96
3			80
4			82
5			95
6			99
7			95
8			100
9			92
10			100

[a] 1 mmol substrate, 4 mmol (30% w/v) H_2O_2, 4 μmol $(NH_4)_7Zn_{0.5}[\alpha\text{-}ZnO_4W_{11}O_{30}ZnO_5(OH_2)]\cdot nH_2O$, 5 mL water, 353 K, 10 h, with vigorous stirring. Conversions were determined by GC and/or proton NMR

Finally, the extent to which the aqueous solution of **1** could be recycled without any significant deterioration in its catalytic performance has been tested. The reactions chosen for these studies were the oxidations of pyridine and diphenyl sulfide to pyridine oxide and diphenyl sulfone, respectively.

The reactions have been carried out in a batch-wise manner by separating the organic layer at the end of each batch, and by adding fresh organic substrate and H_2O_2 for the next batch. The total turnovers over four batches (three recycles) are high, 820 and 545 for diphenyl sulfide and pyridine, respectively.

However, as shown in figure 4, for diphenyl sulfide on recycling some (~ 5–10%) loss in activity is observed. The loss in activity is more pronounced (~ 10–25%) in the case of pyridine. Two possible reasons may be considered for this loss in activity. Small amounts of **1** may be physically lost during each recycle either due to slight solubility in the organic layer or due to handling. Alternatively, **1** may undergo partial deactivation during catalysis. Quantitative estimation of tungsten shows that for both the reactions at the end of the fourth batch only ~ 1% of tungsten is lost. This suggests that deactivation of the catalyst rather than physical loss of the polyoxo compound is the reason for the observed drop in activity. The IR and UV spectrum of **1**, before and after it has been used as a catalyst (figure 5), lends support to the latter explanation as small but definite changes are observed in the spectral signatures of the used catalyst.

4. Conclusion

An aqueous biphasic reaction system has been developed for the selective oxidation of organic sulfides, pyridines, anilines, benzyl halides and benzyl alcohols by H_2O_2 (30%). The oxidations are catalysed by a easily separated, recyclable, polyoxometallate, $\{(NH_4)_7Zn_{0.5}[\alpha\text{-}ZnO_4W_{11}O_{30}ZnO_5(OH_2)]\cdot nH_2O\}$ (**1**). Analogous polyoxometallates where other transition metals fully or partially replaced zinc are poor catalysts. By controlling the temperature, and the H_2O_2: sulfide molar ratio, organic sulfides can be oxidized to the corresponding sulfoxide or sulfone with high selectivity. A simple kinetic model gives good fit between the experimental data points and the predicted concentration profiles. For the oxidations of benzyl halides and benzyl alcohols to the corresponding aldehydes, unlike the reported H_2O_2/Na_2WO_4 system, the catalytic system described here does not require the use of any phase transfer catalyst. Pyridine derivatives are converted to the corresponding N-oxides and aniline derivatives to the corresponding dimeric azoxy compounds with high yields. The catalyst solution can be recycled

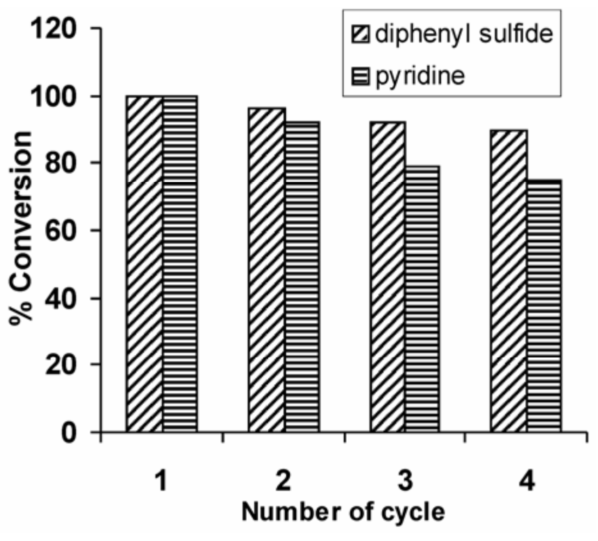


Figure 4. Bar-chart diagram showing recyclibility of **1** for the oxidation of pyridine and diphenyl sulfide.

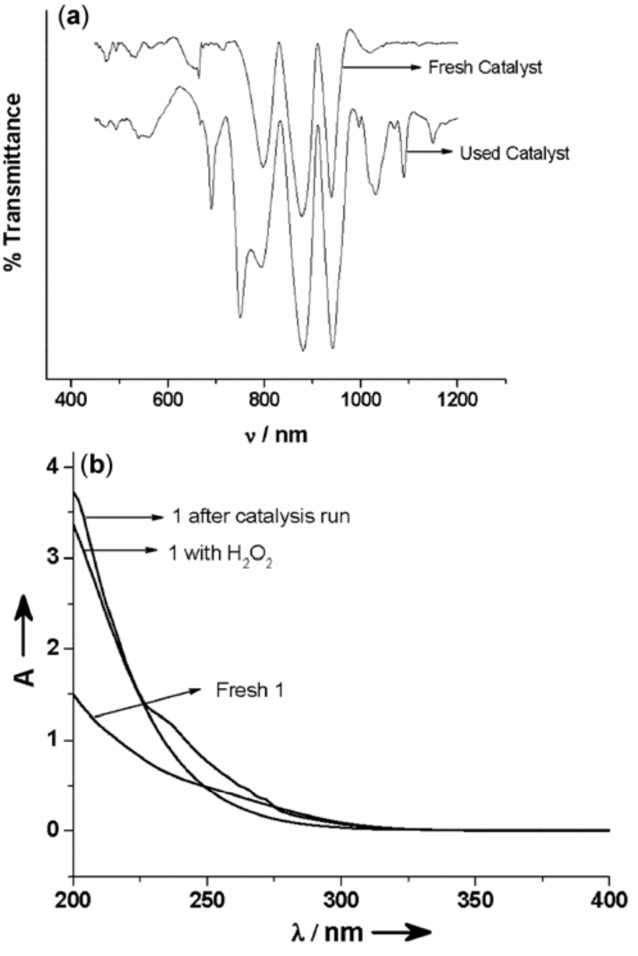


Figure 5. (**a**) IR spectra of (**1**) as KBr disk before and after catalytic run and (**b**) UV spectra of (**1**) in water before and after catalytic run.

several times with low-to-moderate loss in catalytic activities.

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