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# Silica-bound decatungstates as heterogeneous catalysts for $H_2O_2$ activation in selective sulfide oxidation

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**Abstract**

Alkylammonium decatungstates were covalently anchored to silica gel, furnishing efficient and robust heterogeneous catalysts able to activate $H_2O_2$ in the selective oxidation of sulfide to sulfoxide. The organic–inorganic hybrid materials were fully characterized, particularly by spectroscopic experiments. Primary propylammonium decatungstate was the most active catalyst. The use of low amounts of the heterogeneous catalyst (0.1 mol%) with a slight excess of 30% $H_2O_2$ (1.15 equiv.) in a nonchlorinated solvent (methanol) makes this oxidation reaction an environmentally benign chemical process. Leaching and recycling experiments revealed that the supported catalyst is not only highly efficient but also robust, because it can be used six times without loss of activity. Furthermore, the immobilized catalyst can tolerate different types of reaction solvents. Finally, this procedure was successfully applied to various sulfides, including allyl phenyl sulfide and dibenzyl sulfide.

*Keywords:* Heterogeneous catalysis; Decatungstate; Silica-supported decatungstate; Sulfide oxidation; Hydrogen peroxide activation

## 1. Introduction

Oxidation reactions are some of the most useful chemical transformations despite the fact that they are among the most problematic processes, due mainly to the production of large amounts of pollutant materials [1]. At the international level, significant effort has been devoted to substituting the traditional stoichiometric inorganic oxidants such as Cr(VI) and Mn(VII) with cleaner catalytic systems. The heavy metal oxidants give toxic wastes, organic stoichiometric oxidants are usually very expensive [2], and nitric acid unavoidably forms various nitrogen oxides.

Therefore, the need for cleaner and safer oxidation procedures has prompted industrial and academic researchers to investigate the use of benign, easy-to-handle oxidants, such as hydrogen peroxide and molecular oxygen. Indeed, the use of hydrogen peroxide as an oxidant has attracted considerable attention in recent years [3]. Aqueous hydrogen peroxide is an ideal oxidant for liquid-phase reactions because it produces only harmless water by reaction, is safe to store and use, and is cheap and readily available.

Among the different metal catalysts, various types of tungsten-based catalytic systems have been reported to be used in the activation of $H_2O_2$ [4]. Recently, Noyori and co-workers described the activity of sodium tungstate combined with phenylphosphonic acid and a quaternary ammonium hydrogen sulfate as a phase-transfer catalyst [3a,5] in the oxidation of alcohols, olefins, and sulfides.

A further step in the development of environmentally benign chemical processes is the replacement of current homogeneous oxidation procedures for the synthesis of fine chemicals by heterogeneous processes. Immobilized catalysts have been of great interest due to several advantages, such as simplified product workup, separation, isolation, and catalyst reuse [6]. Indeed, chemical processes with little waste are expected from using immobilized catalysts, because these catalysts can be easily recovered and reused.

Further developing our interest in heterogeneous catalysis [7], in this work we present the preparation of alkyl ammonium decatungstates chemically bound to silica support. We explore the activity of these hybrid catalysts in $H_2O_2$ activation, examining the sulfide oxidation as a model reaction.

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Organosulfur compounds are versatile and useful intermediates in organic synthesis for the preparation of biologically active products [8]. The sulfoxide group is present in well-known drugs, the proton-pump inhibitors omeprazole and lansoprazole, as well as in the pesticide fipronil and various insecticides. The selective oxidation of sulfides to sulfoxides is a problem that remains the subject of intensive study [3e,9].

Polyoxometalates, high-valent early-transition metal–oxygen anion clusters, compose a large class of inorganic compounds with significant applications in several areas [10]. One of the most extensively studied applications of polyoxometalates has been in catalysis, where their use as both Brönsted acid catalysts and oxidation catalysts began in the late 1970s [11]. Different types of polyoxometalates have been used for oxidative transformation with various oxygen donors. Oxidation reactions with molecular oxygen and hydrogen peroxide as "green" methods for organic synthesis have gained significant impetus over the past decade [12].

The activity of the decatungstate anion $W_{10}O_{32}^{4-}$ in promoting photo-oxygenation of various substrates has been studied extensively [11b,13]. Recently, hexadecyl trimethyl ammonium decatungstate was reported to catalyze hydrogen peroxide activation for the oxidation of alcohols [14], and a paper dealing with lacunary polyoxotungstate for microwave-assisted $H_2O_2$ activation has been published recently [15].

Heterogenized alkylammonium decatungstates were previously reported in the literature as catalysts for photo-oxidation reactions, but the immobilization of such catalysts was usually performed by impregnation of the solid support [7,13c,16] or by embedding in different polymeric membranes [13a,17a] or inside the silica network [17b]. To enhance the activity and stability, it may be preferable to anchor the metal catalyst to the support through a chemical bond. Thus, we designed an ammonium cation to bound covalently to the solid support and then to introduce the polyoxoanion via an exchange reaction [18]. The anchoring of the metal catalyst through a chemical bond should expand the range of possible reaction solvents to include those solvents able to dissolve and to remove the ammonium decatungstate from the support. Furthermore, the chemical bond, being stronger than electrostatic interactions, should increase the robustness of the catalyst, making it reusable.

In this paper we describe the preparation of various alkylammonium decatungstate catalysts immobilized on silica support.

## 2. Experimental

### 2.1. Materials

All materials purchased were used as such unless otherwise stated. Starting materials for catalyst preparation: silica gel KG60 (size, 0.040–0.063 mm; surface area, 480–540 $m^2/g$; pore volume, 0.74–0.84 $cm^3/g$) for column chromatography (Merck), (3-aminopropyl)triethoxysilane (99%, Aldrich), (3-diethylaminopropyl)trimethoxysilane (⩾90%, Fluka), [3-methylaminopropyl]trimethoxysilane (⩾97%, Fluka), (3-bromopropyl)trimethoxysilane (⩾97%, Fluka), trifluoromethanesulfonic acid (⩾98%, Fluka), sodium tungstate dihydrate (Aldrich). $(n\text{-}Bu_4N)_4W_{10}O_{32}$ was prepared according to a literature procedure [19] and the adsorbed catalyst was prepared following an "impregnation" procedure described previously [7a].

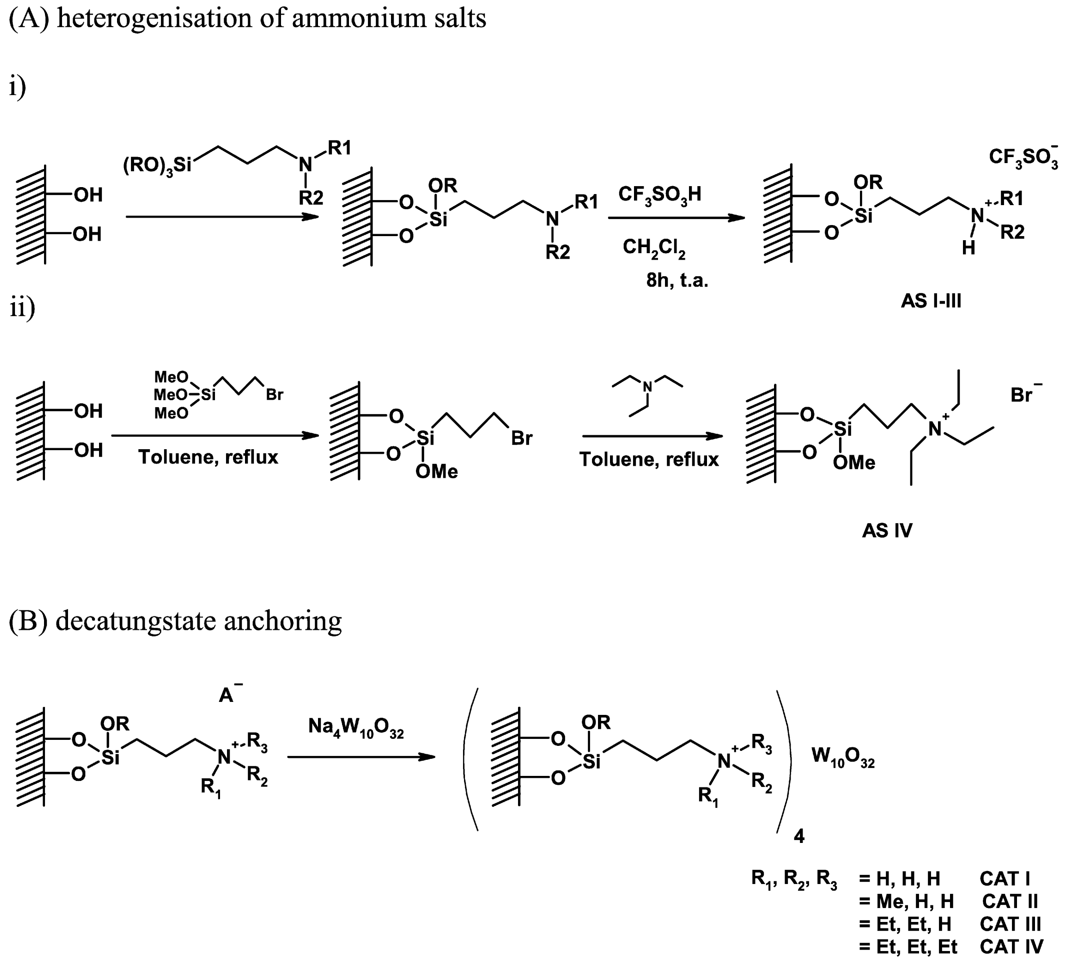
$Na_4W_{10}O_{32}$ was prepared following a literature procedure [13h], adding 260 mL of a boiling aqueous 1 M HCl solution to a boiling solution containing $Na_2WO_4\cdot 2H_2O$ (44 g) in distilled water (250 mL). The resulting solution was allowed to boil for 40 s, after which it was transferred to a 2-L beaker and rapidly cooled to 0 °C in a liquid nitrogen/acetone bath under stirring. Solid NaCl was added to saturation while the temperature was maintained at 0 °C. A precipitate formed that was collected on a fritted funnel; washed in a small amount of cold water, ethanol, and diethyl ether; and transferred to a 250-mL beaker. (The use of nonmetallic spatula is recommended to avoid the formation of a blue color.) This precipitate was suspended in hot acetonitrile (130 mL); then the suspension was filtered, and the filtrate was placed in a freezer overnight. Large pale-lime crystals of sodium decatungstate were collected on a fritted funnel and dried (9.4 g). From the mother liquor, it was possible to obtain more crystals on concentration. The absorbance spectrum in acetonitrile or in water comprised a well-defined maximum at 324 or 323 nm, respectively.

The starting materials for sulfide oxidation were hydrogen peroxide (30%, Carlo Erba), methyl phenyl sulfide (99%, Aldrich), methyl-4-methoxyphenyl sulfide (97%, Aldrich), methyl-4-bromophenyl sulfide (97%, Aldrich), dibenzyl sulfide (⩾95%, Fluka; it was recrystallized from diethyl ether), diphenyl sulfide (98%, Aldrich), and allyl phenyl sulfide (⩾96.5%, Fluka).

### 2.2. Catalyst preparation

The preparation of catalysts **CAT I–IV** involved two main steps: (a) silica functionalization anchoring ammonium salts to surface silanols and (b) anion exchange with sodium decatungstate (Scheme 1). Silica was activated by refluxing in HCl conc. for 4 h, followed by washing until neutral with distilled water and then drying [20]. Alkylammonium heterogenization was done by one of two procedures depending on the type of ammonium cation.

Anchored primary, secondary, and tertiary ammonium salts were prepared by refluxing activated silica (5 g) and the suitable (alkylaminopropyl)trialkoxysilane (10 mmol) in toluene (30 mL) under stirring for 1 h. After distillation of a toluene fraction containing ethanol, the refluxing was continued. After 1 h, this second procedure was repeated and refluxing continued for 0.5 h [21]. The cooled functionalized silica was filtered off; washed with toluene, diethyl ether, and dichloromethane (2 × 25 mL each); and then dried under high vacuum at 60 °C for 3 h to give the surface-bound alkylamine groups with a loading of 0.8–0.9 mmol/g. The resulting materials in dry dichloromethane (5 g in 25 mL) were reacted with trifluoromethane sulfonic acid (two equivalents with respect to the supported amino group) for 8 h at room temperature; filtered off; washed successively with dichloromethane, ethanol, and diethyl ether (2 × 25 mL each) [18a]; and then dried under vacuum at 60 °C for 3 h, affording the corresponding alky-



Scheme 1.

lammonium salts bound to the solid surface (**AS I–III** in Scheme 1, Ai). Elemental analyses revealed a sulfur loading of 0.8–0.9 mmol/g.

To prepare supported quaternary ammonium bromide, (3-bromopropyl)trimethoxysilane (2.43 g, 10 mmol) was condensed with 5 g of silica silanols by refluxing in 30 mL of toluene following the procedure described above. The bromopropylated silica (5 g, 0.5 mmol/g loading) was then treated with triethylamine (1.01 g, 50 mmol) in 30 mL of refluxing toluene for 24 h, affording the corresponding supported quaternary ammonium bromide (**AS IV** in Scheme 1, Aii) [22]. After cooling, the solid was filtered on a Büchner funnel and carefully washed with toluene (5 × 20 mL), then dried at 60 °C under high vacuum. The amount of bromide ions present on the functionalized silica after the reaction with triethylamine was determined by titration [21] according to the method described by Volhard, starting from 0.30 g of immobilized salt in 10 mL of ethanol, 10 mL of 0.1 N $AgNO_3$ solution, and 5 mL of $HNO_3$ 6 N were added, and the suspension was stirred in the dark for 0.5 h at room temperature. Then the solid was filtered off, and the excess $AgNO_3$ was titrated with 0.1 N ammonium thiocyanate, giving a bromide loading of 0.43 mmol/g.

The catalysts **CAT I–IV** were prepared by stirring a mixture of the selected surface-bound alkylammonium salt (4 mmol) and an aqueous solution of sodium decatungstate (4 mmol) in distilled water at room temperature for 30 min (Scheme 1, B). For example, supported propylammonium triflate **AS I** (5 g, loading 0.80 mmol/g) was stirred with sodium decatungstate (9.77 g, 4.0 mmol) in 30 mL of distilled water. The choice of the reaction time is important to ensure the anion exchange avoiding the degradation of sodium decatungstate in water as evidenced by following the variation of the UV absorption band at 323 nm. After stirring, the white solids were filtered off, carefully washed with 700 mL of distilled water, 50 mL of ethanol, and 50 mL of diethyl ether. Then they were washed in continuous with hot acetonitrile for 12 h using a Soxhlet apparatus. After drying at 60 °C under high vacuum for 3 h, the catalysts were completely characterized.

### 2.3. *Catalyst characterization*

All functionalized materials were characterized with respect to compositional, structural, and surface properties. The loading of the organic groups was calculated by elemental analysis performed with a Carlo Erba CHNS-O EA1108 elemental analyzer. Metal elemental analyses were performed by ICP-AES on an Ultima 2 Jobin Yvon HORIBA instrument, with testing solutions prepared by dissolving about 5 mg of the catalyst in

10 mL of 10% dilute $NH_4OH$ and further diluting by 1:10 with distilled water. (It is important that these solutions be transferred quickly in PE vials when Na is determined, to avoid contamination from glass.) EDS analyses of the catalysts, in a windowless configuration, to determine the presence of sodium and tungsten were performed in a Philips 515 scanning electron microscope equipped with an EDAX Phoenix microanalyzer.

Thermogravimetric analysis and differential thermal analysis (TGA–DTA) were carried out on a Perkin–Elmer TGA7 analysis system. $N_2$ adsorption–desorption isotherms, obtained at 77 K using a Micrometrics PulseChemiSorb 2705, were used to determine specific surface areas, $SA_{\mathrm{BET}}$. Before each measurement, the samples were outgassed at 383 K for 1 h. FTIR spectra of all of the catalysts (KBr pellets) were recorded on a Nicolet FTIR Nexus spectrophotometer (resolution 4 $cm^{-1}$) in the range of 4000–400 $cm^{-1}$. DRS-UV measurements were performed using a Varian 2390 UV–vis spectrophotometer equipped with an integrating sphere in the range of 220–500 nm.

### 2.4. Reaction procedure for sulfide oxidation

Typical oxidation of methyl phenyl sulfide with hydrogen peroxide as model reaction was performed using a round-bottomed flask. The selected catalyst (the amount of which was evaluated on the basis of loading values for introducing the specified amount of decatungstate) and 30% $H_2O_2$ (0.23 mL, 2.30 mmol) were added to a solution of methyl phenyl sulfide (0.25 g, 0.23 mL, 2.0 mmol) in the specified solvent (10 mL). The reaction was stirred at room temperature for 1.5 h. The progress of the oxidation reaction was monitored by GC and TLC. After 1.5 h, the mixture was filtered on Büchner funnel. The solid catalyst was washed with 5 mL of methanol and recovered. When the $CH_2Cl_2$/MeOH mixture was used as reaction solvent, distilled water was added to the solution to obtain phase separation, and further extraction was accomplished with $CH_2Cl_2$ (2 × 10 mL). When the reaction solvent was MeOH, the solution was rapidly evaluated by gas chromatography; otherwise, $Na_2S_2O_3$ was added to the solution to consume the excess $H_2O_2$ (verified by an iodinated paper test) and filtered off [5]. The gas-chromatographic analyses were performed on a TraceGC ThermoFinnigan instrument with a Supelco SPB-20 fused silica capillary column (30 m × 0.25 mm) with helium as a carrier, adding 4-*tert*-butylphenol as an internal standard.

The hydrogen peroxide content in the reaction mixture was measured following a standard iodometric titration method with sodium thiosulfate [23]. The model reaction of methyl phenyl sulfide and hydrogen peroxide was monitored between 10 and 120 min. Samples were obtained periodically, and the course of the reaction was followed by gas chromatography using 4-*tert*-butylphenol as the internal standard added to the samples.

The same methodology was followed in the synthetic application to different sulfides using the best catalyst **CAT I**. The products were purified by flash chromatography over silica gel column, using hexane–ethyl acetate mixtures as eluants. All products gave melting points and spectral data consistent with those reported.

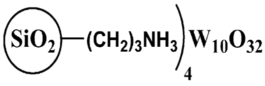
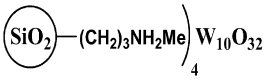
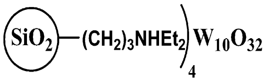
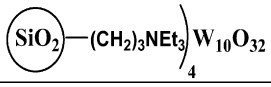
## 3. Results and discussion

### 3.1. Catalyst characterization

Table 1 summarizes the BET surface areas. As expected, a general decrease in surface area was found due to functionalization, and a more pronounced effect was observed with increasing of loading. Elemental analysis of the materials obtained at each step of functionalization allowed us to evaluate the loading of the supported organic moieties, which was found to be 0.3–0.9 mmol/g. The higher values of loading observed at the first step when propylamino groups were present could be ascribed to base catalyzed condensation. The absence of sulfur atoms after the exchange process is noteworthy, indicating the complete substitution of trifluoromethane sulfonate with decatungstate anions.

ICP-AES analyses of the catalysts allowed us to evaluate the W loading. The $W_{10}$ loading of catalysts **CAT I–IV** are reported in Table 1. The simultaneous ICP-AES analyses of W and Na demonstrated that practically all of the sodium of $Na_4W_{10}O_{32}$ was exchanged. The complete substitution of sodium in supported decatungstate was confirmed by EDS mi-

Table 1
Surface area ($SA_{\mathrm{BET}}$), $A^-$ loading in precursor **AS**, N and decatungstate loading of catalysts **CAT I–IV**

| Catalyst | | $SA_{\mathrm{BET}}$ ($m^2/g$) | $A^-$ load. in **AS** (mmol/g) | N loading (mmol/g) | $W_{10}$ loading (mmol/g) |
|---|---|---|---|---|---|
| **CAT I** |  $(\mathrm{SiO_2{-}(CH_2)_3NH_3})_4W_{10}O_{32}$ | 190 | 0.80 | 0.7 | 0.12 |
| **CAT II** |  $(\mathrm{SiO_2{-}(CH_2)_3NH_2Me})_4W_{10}O_{32}$ | 173 | 0.92 | 0.7 | 0.16 |
| **CAT III** |  $(\mathrm{SiO_2{-}(CH_2)_3NHEt_2})_4W_{10}O_{32}$ | 185 | 0.81 | 0.6 | 0.13 |
| **CAT IV** |  $(\mathrm{SiO_2{-}(CH_2)_3NEt_3})_4W_{10}O_{32}$ | 313 | 0.43 | 0.3 | 0.06 |

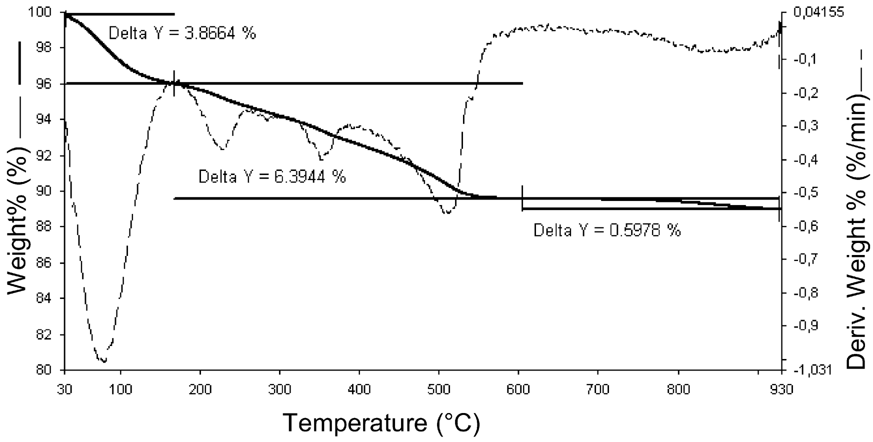


Fig. 1. TGA/DTG analysis of **CAT I**.

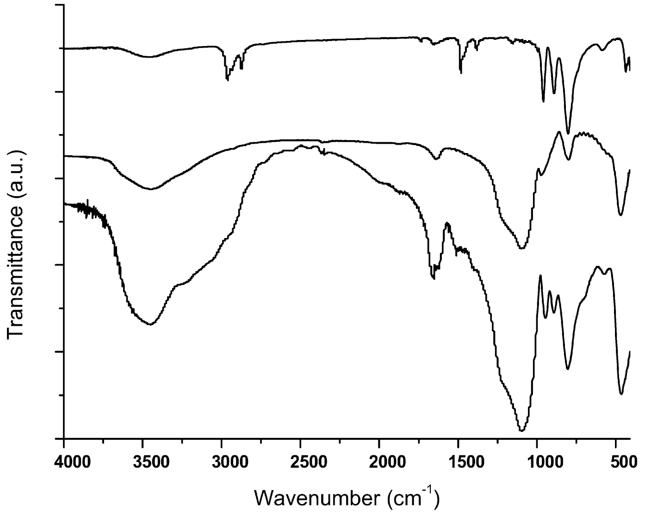


Fig. 2. FT-IR spectra of (a) $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$; (b) bare $SiO_2$; (c) **CAT I**.

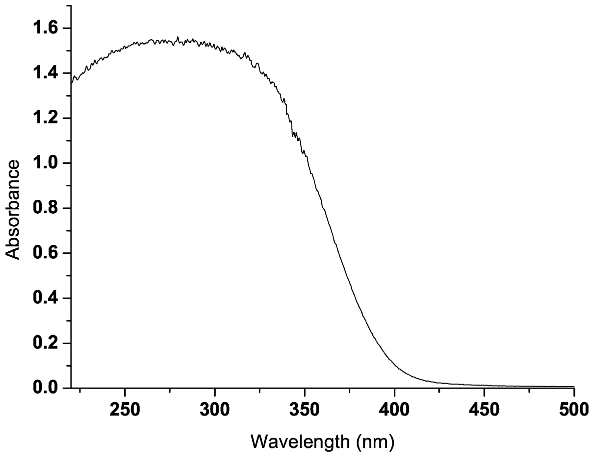


Fig. 3. Diffuse reflectance UV–vis spectrum of **CAT I**.

croanalysis. The discrepancy between nitrogen and $W_{10}$ loadings is not as high as it might appear, because one decatungstate unit requires four ammonium cations. In addition, we verified that silica treated with $Na_4W_{10}O_{32}$ and washed according to the exchange procedure did not present any amount of tungsten. This result indicates that the only species present on silica are alkylammonium decatungstates bound to the support.

TGA/DTG of all of the catalysts revealed that the first step of thermal decomposition, from room temperature to 170 °C, corresponds to removal of the surface-adsorbed water, and that the major weight loss occurs at high temperature, as expected for chemisorbed materials, confirming that ammonium groups are covalently bound on the surface of silica. Fig. 1 shows the TGA/DTG results for **CAT I**.

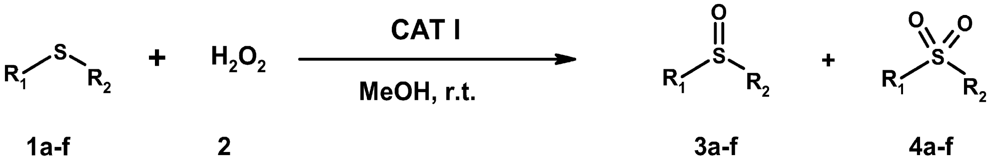
FTIR spectra demonstrate that the structure of decatungstate was still preserved on the silica surface. The characteristic frequencies of W–O stretching modes [19,24a] were observed for all the catalysts. Fig. 2 shows the spectra of the bare $SiO_2$ (a), $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ (b), and **CAT I** (c), in which the three bands at 945, 893, and 803 $cm^{-1}$ are readily distinguishable.

UV–vis spectroscopy is reported highly diagnostic for decatungstate polyanion [13h,24], showing a characteristic absorption at 324 nm (in addition to the band at 268 nm) in solution assigned to oxygen-to-tungsten charge transfer (O → W CT) transition. The UV–vis diffuse reflectance spectra of all of the catalysts showed this typical band. Fig. 3 illustrates the spectrum of **CAT I**.

### 3.2. *Catalytic activity*

The catalytic activity of the heterogenized decatungstates was tested in the oxidation of sulfides. The oxidation of phenyl methyl sulfide with 30% $H_2O_2$ was selected as the model reaction (Scheme 2). A $CH_2Cl_2/CH_3OH$ (1:1) mixture was first chosen as reaction solvent because it gives a homogeneous phase with the reagents, increasing the accessibility to the catalyst, and avoids reagent/product adsorption on the solid support, as was reported recently [18a].

We examined the catalytic activity of **CAT I** reacting methyl phenyl sulfide (2 mmol) and 30% $H_2O_2$ in $CH_2Cl_2/CH_3OH$ (1:1) (10 mL) at room temperature for 1.5 h. The amounts of catalyst and hydrogen peroxide were varied to use the minimum amount of each. The data, reported in Table 2, reveal that **CAT I** is very active. Indeed, using a very low quantity (0.1 mol%) of decatungstate with respect to sulfide, methyl phenyl sulfoxide



Scheme 2.

Table 2
Methyl phenyl sulfoxide synthesis[a] catalyzed by **CAT I**

| Entry | **CAT I** (mol%) | Ratio **1:2** | **3** yield (%) | **3** selectivity (%) | TON[b] |
|---|---|---|---|---|---|
| 1 | 2 | 1:1.0 | 93 | 94 | 49 |
| 2 | 0.5 | 1:1.1 | 88 | 96 | 185 |
| 3 | 0.2 | 1:1.1 | 85 | 96 | 445 |
| 4 | 0.1 | 1:3.0 | 89[c] | 91[c] | 980 |
| 5 | 0,1 | 1:1.15 | 92 | 95 | 960 |
| 6 | $SiO_2$ | 1:1.15 | 2 | – | – |

[a] Reactions were performed reacting sulfide 2 mmol and 30% $H_2O_2$ in $CH_2Cl_2/CH_3OH$ (1:1) (10 mL) for 90 min.

[b] Turnover number calculated as products (mol)/catalyst (mol).

[c] Reaction time 60 min, then the selectivity decreased.

Table 3
Effect of ammonium cation in **CAT I–IV** activity[a]

| Entry | CAT | **3** yield (%) | TON[b] |
|---|---|---|---|
| 1 | **CAT I** | 92 | 960 |
| 2 | **CAT II** | 49 | 515 |
| 3 | **CAT III** | 32 | 333 |
| 4 | **CAT IV** | 30 | 315 |
| 5 | **CAT IV** | 87[c] | 50 |

[a] Reactions were performed reacting sulfide 2 mmol, 30% $H_2O_2$ 2.3 mmol, catalyst 0.1 mol% (0.002 mmol of $W_{10}$) in $CH_2Cl_2/CH_3OH$ (1:1) (10 mL) for 90 min.

[b] Turnover number calculated as products (mol)/catalyst (mol).

[c] Catalyst 2 mol%.

was obtained at a 92% yield and 95% selectivity (Table 2, entry 5).

A slight excess of $H_2O_2$ (1.15 equiv.) was used when the amount of catalyst was decreased. Using a greater amount of $H_2O_2$ (3 equiv.) allowed us to obtain a high yield (89%) with good, but decreased selectivity (91%) in a shorter time (1 h) (Table 2, entry 4), after which the selectivity decreased due to further oxidation to sulfone. Aiming to reduce the waste of reagent, we used 1.15 equiv. of $H_2O_2$.

To investigate the possible influence of the solid support on the reaction outcome, a blank reaction was carried out adding unfunctionalized silica. Only traces (2%) of sulfoxide were obtained (Table 2, entry 6).

The different catalysts **CAT I–IV** were tested to examine the possible influence of the ammonium cation on the polyoxometalate activity. The amount of catalyst used in each experiment was determined based on the loading value to introduce the same supported decatungstate equivalents (0.1 mol%). The data reported in Table 3 demonstrate a strong effect of the ammonium cation. The catalyst containing primary ammonium cation, **CAT I**, is the most active, giving phenyl methyl sulfoxide at a very high yield and selectivity, followed by **CAT II**, which contains a secondary ammonium group. We can attribute this effect to the increasing steric hindrance of the ions surrounding decatungstate, which make it less accessible. Prompted by the high selectivity ($\geqslant$95%) observed for all of the catalysts, we checked whether increasing the amount of **CAT IV** (2 mol%) would produce more sulfoxide **3a** in a shorter time, due to the increased number of catalytic sites in the reaction. After 45 min, the conversion was 95 with 96% selectivity. The selectivity decreased during the time due to overoxidation; after 90 min, it was 87% with complete conversion (Table 3, entry 5). However, the TON values indicate increasing the amount of catalyst decreased the efficiency, as sometimes occurs [26]. Therefore, we found that all of the catalysts prepared were able to promote the oxidation of sulfide **1** by hydrogen peroxide, increasing only the relative amount.

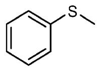
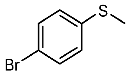
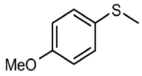
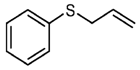
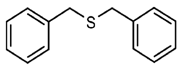
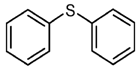
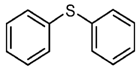
In an attempt to develop an environmentally friendly process, we tried to avoid using chlorinated solvent. We succeeded in accomplishing the reaction solely in methanol with good results, obtaining the solfoxide at 92% yield and 97% selectivity (Table 4, entry 1). We also carried out the model reaction in isopropanol and acetonitrile as solvents and achieved the expected sulfoxide **3a** yields of 86 and 80%, respectively. These findings demonstrate that methanol was the best reaction solvent. We performed some experiments using 10% $H_2O_2$ and obtained lower conversions (75% after 90 min and 83% after 120 min) with high selectivity (96%). This negative role of water can be attributed to competitive interaction with the metal and to modification of the polarity of the catalyst surface. Indeed, the increased surface hydrophobicity can decrease the reactivity of the hydrophobic sulfide reagent.

The conversion and product distribution of the model reaction were determined as functions of the reaction time (Fig. 4). The results demonstrate that sulfoxide **3a** was formed selectively and the amount of sulfone **4a** increased slightly increased over time. It is interesting to note that sulfone **4a** can be obtained selectively (100%) in a quantitative yield reacting the sulfide **3a** with 3 equivalents of 30% $H_2O_2$ in the presence of **CAT I** (1 mol%) for 4 h (Table 4, entry 2).

The possible hydrogen peroxide decomposition was examined both in the reaction mixture and in a blank experiment in which hydrogen peroxide was stirred in the presence of **CAT I** in methanol for 90 min. A hydrogen peroxide efficiency of 95–98% was found, indicating that unproductive decomposition was negligible.

To explore the general applicability of this reaction, we examined various sulfides. As reported in Table 4, variously substituted aryl methyl sulfides underwent smooth oxidation to selectively afford the corresponding sulfoxides in high yields (Table 4, entries 1–3). The selective oxidation of allyl phenyl sulfide to the corresponding sulfoxide (Table 4, entry 4) is note-

Table 4
Oxidation of sulfides **1** to sulfoxides **3** using 30% $H_2O_2$ catalyzed by **CAT I** in MeOH[a]

| Entry | Sulfide | Product | **3** yield (%) | **3** selectivity (%) | TON[b] |
|---|---|---|---|---|---|
| 1 |  | **3a**[c] | 92 | 97 | 953 |
| 2 |  | **3b** | 80 | 95 | 842 |
| 3 |  | **3c** | 86 | 97 | 890 |
| 4 |  | **3d** | 83 | 96[d] | 865 |
| 5 |  | **3e** | 94[e] | 94[e] | 995 |
| 6 |  | **3f** | 56 | 95 | 588 |
| 7 |  | **3f** | 90[f] (85)[g] | 90[f] (96)[g] | 995 (443) |

[a] Reactions were performed reacting sulfide 2 mmol, 30% $H_2O_2$ (1.15 equiv.), catalyst 0.1 mol% in $CH_3OH$ (10 mL) for 90 min.

[b] Turnover number calculated as products (mol)/catalyst (mol).

[c] When the reaction was carried out using 30% $H_2O_2$ (3 equiv.) and catalyst 1 mol% for 4 h the corresponding sulfone **4a** was obtained in 99% yield and 100% selectivity.

[d] No epoxidation product was detected.

[e] Evaluated by $^1$H NMR.

[f] Reaction time 24 h.

[g] Reaction time 6 h using catalyst 0.2 mol%.

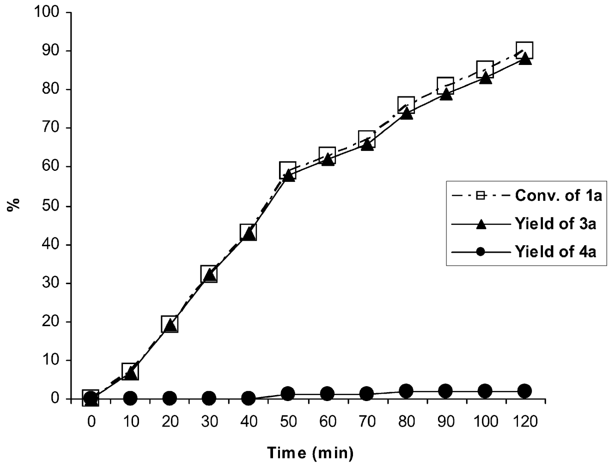


Fig. 4. Reaction profile of the oxidation of methyl phenyl sulfide **1a** over **CAT I**.

worthy. Epoxidation of the double bond was not observed, and the corresponding sulfoxide was obtained in good yield and selectivity.

A surprising result was the selective oxidation of dibenzyl sulfide (Table 4, entry 5). Indeed, it has been reported that the oxidation of dialkyl sulfides leads to the formation of sulfones along with sulfoxides with poor selectivity [3e,18a].

It is known that the formation of sulfoxides from diaryl sulfides is difficult to achieve using 30% $H_2O_2$ [5,18a]. Interestingly, under the described reaction conditions, even diaryl sulfide furnished the corresponding sulfoxides in very good yield in a reaction carried out for 24 h, or for 6 h in the presence of 0.2 mol% of catalyst (Table 4, entry 7). A possible mechanism of this reaction involves the formation of peroxotungstate species [15,25] and the subsequent nucleophilic attack of the sulfur atom in the thioether on the peroxo species. Indeed, it is known that thioethers are oxidized to sulfoxides by electrophilic oxidants [27], which explains the minor reactivity of aromatic thioethers, as found in other studies [28], due to delocalization of the electron density on the sulfur.

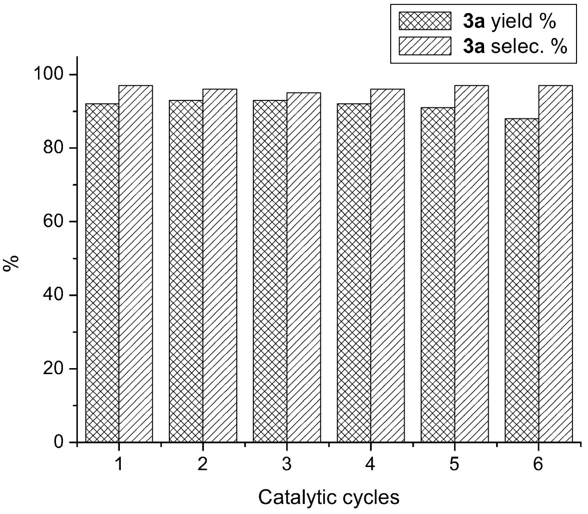


Fig. 5. Catalyst recycling in methyl phenyl sulfide oxidation.

Considering our results all together, we can conclude that heterogenized decatungstate **CAT I** is very efficient in the activation of hydrogen peroxide in sulfide oxidation. This catalyst also shows high hydrogen peroxide efficiency for the reaction studied.

### 3.3. *Leaching test and recycling*

To verify the heterogeneity of the catalytic process, we performed the leaching test suggested by Lempers and Sheldon [29]. The reaction was filtered after 15 min, and stirring was continued for 75 min after the catalyst was removed. The reaction yield did not change significantly (from 18 to 21%), indicating that no leaching of the active catalytic species occurred during the reaction. It is noteworthy that in contrast, the $(Bu_4N)_4W_{10}O_{32}$ adsorbed on silica gave a positive leaching test, with the product yield increasing from 20 to 60% after filtration.

Finally, we carried out recycling experiments for the oxidation of methyl phenyl sulfide **1a** in methanol (Fig. 5). The filtered catalyst was dried after washing and reused without further activation. Interestingly, the recycled catalyst could be reused for at least five reaction cycles with almost unchanged results. For comparison, the adsorbed decatungstate demonstrated a dramatic drop in yield (from 92 to 16%) during the second cycle.

## 4. Conclusion

Heterogenized ammonium decatungstates bound to silica support were developed by an exchange process on anchored alkylammonium cations and used as catalysts to activate hydrogen peroxide in sulfide oxidation. Spectroscopic studies demonstrated that the decatungstate structure was preserved in the catalysts. The best catalyst, **CAT I**, was very efficient, giving methyl phenyl sulfoxide in high yield (92%) and selectivity (95%) under mild heterogeneous conditions. Our goal of obtaining a robust catalyst linking the polyoxometalate to the solid support by chemical bonds rather than by simple electrostatic interactions was achieved. Indeed, Sheldon's test demonstrated that no leaching of the active species occurred and the catalyst could be reused at least five times. Furthermore, different reaction solvents could be used without removing the decatungstate from the support. In addition, there is the advantage of easy separation and recovery of the heterogeneous catalyst.

The oxidation procedure using **CAT I** is of general applicability to various sulfides with very good yields and selectivities that are similar or higher than those reported in the literature. Moreover, this catalyst shows high hydrogen peroxide efficiency for the reaction studied.

The use of a low amount of heterogeneous catalyst (0.1 mol%) and a slight excess of $H_2O_2$ (1.15 equivalent) in a nonchlorinated solvent, along with the absence of additives (such as soluble phase transfer catalyst) or cocatalyst (such as $C_6H_5$–$PO_3H_2$) makes this oxidation reaction an environmentally benign chemical process.

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