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Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Synthesis, characterization of a Sb(V)-containing polyoxomolybdate serving as a catalyst for sulfoxidation

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A Sb-containing Anderson-based polyoxomolybdate cluster, $[(CH_3)_4N]_4H_8[Na_5Sb_3(Sb_2Mo_{12}O_{57})]\cdot17H_2O$ [1; $(CH_3)_4N^+ = TMA^+]$, has been successfully synthesized by using an aqueous solution method and structurally characterized. In particular, UV-Vis spectroscopy has been employed to elucidate the stability of polyoxoanion. Under mild conditions, the catalyst demonstrates high activity and selectivity for the sulfoxidation of various sulfides in the presence of hydrogen peroxide. For example, thioanisole undergoes up to 100% conversion and 100% sulfone selectivity at 25 °C in aqueous solution.

Introduction

Sulfoxidation is one of the basic and important reactions in organic synthesis. Sulfoxides and sulfones as the oxidation products are widely utilized as fine synthetic reagents for the synthesis of new drugs,¹ as ligands for transition metal asymmetric catalysis,² and as oxotransfer reagents in oxidation processes.³ Moreover, sulfoxidation is also the basis for the catalytic oxidative desulfurisation of crude oil to remove sulfur-based impurities as the resulting sulfones can be selectively extracted into a polar solvent under milder conditions than those traditionally required for industrial catalytic hydrodesulfurisation.⁴ Hereto, a wide variety of oxidizing agents have been used in those preparative processes such as nitric acid, K₂FeO₄, oxone, hypervalent iodine, UHP, solid oxidizing agents, etc.⁵ Unfortunately, most of the systems reported so far often suffer numerous drawbacks in terms of low yields, poor E-factors, complex handling procedures and extreme reaction conditions. With the increasing environmental and economical concerns in recent years, benign oxidization reaction using H₂O₂ as terminal oxidant would be promising because only water is produced as the sole by-product.⁶ Additionally, as part of "green" concept, toxic organic solvents are expected to be replaced by alternative non-toxic media. Water undoubtedly is a unique solvent thus oxidations of sulfides in aqueous media rather than in common poisonous organic solvents are highly

mandatory to implement in daily concerns.⁷ It will be a meaningful approach to accomplish green industrial goals if insoluble organic substrates could be oxidized with hydrogen peroxide in water at mild conditions.

As is well known, the polyoxometalates (POMs) possess interesting electronic properties that implied them as a unique class of molecules having great potential applications in diverse areas such as catalysis, medicine, magnetism, electronics and photochemistry.⁸ In addition, one of the most interesting aspects of POM chemistry lies with the fact that they can be viewed as promising hetro- and homogeneous catalysts because of their reusability, corrosiveness, high thermal stability and oxidative redox properties.9 It is to be noted that Anderson-based polyoxoanions are considered as an important class of POMs family, due to its abundant terminal oxygen atoms with high reactivity since they consist of a single metal atom supported by six-edge sharing MO_6 (M = W or Mo) octahedra.^{10,11} For example, an Anderson-supported polyoxometalate $[(C_4H_9)_4N]_6Mo_7O_{24}$ reported by X. Yang et al was found to be a highly efficient catalyst in the oxidation reaction of sulfides.^{11a} A single-sided triol-functionalized iron-Anderson polyoxometalate, centered $[[N(C_4H_9)_4]_3 [FeMo_6O_{18}(OH)_3\{(OCH_2)_3CNH_2\}]$, can efficiently catalyze the aerobic oxidation of aldehydes in water for the green preparation of carboxylic acids.^{8a}

On the other hand, Sb-containing polyoxomolybdates emerging as a unique branch of POMs, have recently become an area of significant interest on account of their important role in oxidation catalysis systems.¹² Till now, antimony-containing POMs have been extensively studied, however among them mostly are Sb(III)-containing polyoxotungstates such as $[Sb_2W_{22}O_{74}(OH)_2]^{12-,13a} [Sb_2^{III}W_{20}M_2O_{70}(H_2O)_6]^{(14-2n)-} (M = Fe^{3+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+})^{13a}$ and $[Cs_2Na(H_2O)_{10}Pd_3(\alpha-Sb^{III}W_9O_{33})_2]^{9-}$ et al.^{13J} Compared to the numerous Sb(III)-containing polyoxotungstates, there are very few Sb(V)-polyoxomolybdates become apparent since the advent of first

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Electronic Supplementary Information (ESI) available: The bond valence sum calculations (Table S1); Selected bond lengths (Table S2); additional structural figures (Fig. S1–S4); XPRD, IR, and TG (Fig. S5–S7); catalytic properties (Table S3, Fig. S8–S11). CCDC: 1573050. See DOI: 10.1039/x0xx00000x

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Table 1 Summary of Sb-containing POMs

Ref.	Formulas
13a	[Sb ₂ ^{III} W ₂₂ O ₇₄ (OH) ₂] ¹²⁻
13a	$[Sb_2^{III}W_{20}M_2O_{70}(H_2O)_6]^{(14-2n)-}$ (M = Fe ³⁺ , Co ²⁺ , Mn ²⁺ , Ni ²⁺ , Zn ²⁺)
13b	$[Zn_3(H_2O)_3(\alpha-Sb^{III}W_9O_{33})_2]^{12-}$
13c	$[Cu_3(H_2O)_3(\alpha-Sb^{III}W_9O_{33})_2]^{12-}$
13d	$[Sb_6^{III}W_{65}O_{217}(H_2O)_7]^{26-}$
13e	[Fe ₄ (H ₂ O) ₁₀ (β-Sb ^{III} W ₉ O ₃₃) ₂] ⁶⁻
13f	[(Mn(H ₂ O)) ₃ (Sb ^{III} W ₉ O ₃₃) ₂] ¹²⁻
13g	$[Na_2Sb_4(H_2O)_4(Sb^{III}W_9O_{33})_4]^{22-}$
13h	$[Ce_3Sb_4W_2O_8(H_2O)_{10}(Sb^{III}W_9O_{33})_4]^{19-}$
13i	$[(VO)_3(\alpha-Sb^{III}W_9O_{33})_2]^{12-}$
13j	$[Cs_2Na(H_2O)_{10}Pd_3(\alpha-Sb^{III}W_9O_{33})_2]^{9-}$
13k	[(MnCl) ₆ (Sb ^{III} W ₉ O ₃₃) ₂] ¹²⁻
131	$[\{Na(H_2O)_2\}_3\{M(C_3H_4N_2)\}_3(Sb^{III}W_9O_{33})_2]^{9-} (M = Co^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+})$
14	[H ₂ Sb ^v Mo ₆ O ₂₄] ⁵⁻
15a	[PSb ^{III} (H ₂ O)Mo ₁₁ O ₃₉] ⁴⁻
15b	[Sb4 ^V Mo ₁₂ (OH) ₆ O ₄₈] ¹⁰⁻
15c	[Sb4 ^V Sb2 ^{III} MO ₁₈ O ₇₃ (H ₂ O) ₂] ¹²⁻

Sb(V)-containing polyoxomolybdate $[H_2Sb^VMo_6O_{24}]^{5-}$ reported by Sasaki et al in 1982.^{14,15} A comprehensive literature survey of Sb-containing POMs is shown in Table 1.

Thus, the Sb(V)-containing Anderson-based polyoxomolybdates serving as potential catalysts grab our great attention. As expected, a new Sb-containing Anderson-supported polyoxomolybdate cluster, TMA₄ $H_8[Na_5Sb_3(Sb_2Mo_{12}O_{57})]$ ·17H₂O, has been firstly isolated. As an oxidative catalyst, it could be used to the simple, mild, and efficient oxidation of sulfides for the first time. Furthermore, the homogeneous catalyst system can be reused in successive reactions for eleven times.

Experimental

General methods and materials

All chemical reagents were commercially procured and were used without further purification. The Infrared spectra (using KBr in pellets) were recorded on a Bruker VERTEX 70 IR spectrometer in the range of 4000-450 cm⁻¹. Elemental analyses (C, H, and N) were conducted on a PerkinElmer 2400-II CHNS/O analyzer. Inductively coupled plasma (ICP) analyses were performed on a Perkin-Elmer Optima 2000 ICP-OES spectrometer. UV absorption spectra were obtained with a U-4100 spectrometer at room temperature. Thermogravimetry analysis (TGA) was carried out under a nitrogen gas atmosphere on a Mettler-Toledo TGA/SDTA851^e instrument with a heating rate of 10 °C min⁻¹ from 25 to 800 °C. X-ray powder diffraction (XPRD) measurement was performed on a Bruker AXS D8 Advance diffractometer instrument with Cu Ka radiation (λ = 1.54056 Å) in the angular range 2 θ = 5–40° at 293 K. X-ray photoelectron spectra (XPS) were recorded with an Axis Ultra X-ray photoelectron spectrometer. GC chromatogram was carried out on Bruker 450-GC (flame ionization detector) instrument equipped with a 30m column (GsBP-5, 0.25 mm internal diameter and 0.25 um film thickness) with nitrogen as carrier gas.

Synthesis of TMA4H8[Na5Sb3(Sb2M012O57)]-17H2O (1)

(NH₄)₆Mo₇O₂₄·4H₂O (3.2 g, 16.32 mmol) was dissolved in 9 ml H₂O and heated to 50 °C (denoted as solution A). In a separate beaker, Sb₂O₃ (0.607 g, 2.08 mmol) was dissolved in 3 mL of dilute HCl (3.0 M), and then Sb_2O_5 (0.605 g, 1.87 mmol) was added (denoted as solution B). When all the solid materials had been completely dissolved, B was added dropwise to A. After cooling to room temperature, TMAOH (2 mL, 1.1 M) was added to the resulting cyan solution. Subsequently, the pH value of the mixture was carefully adjusted to 5.44 using NaOH (6.0 M) solution. Then after that, the resulting reaction mixture was heated to 60 °C and stirred for 30 min followed by the addition of FeSO₄ solution (2 mL, 0.07 M). Subsequently, the reaction mixture was heated at 60 °C and stirred 30 min again, and then allowed to cool down at room temperature. A clear cyan solution was obtained and filtered to stand for crystallization. Colorless block-shaped crystals were collected after six weeks. Yield: 0.325g. [49.9 % Based on Mo] Elemental analysis (%) calcd: C, 5.66; H, 2.67; N, 1.65; Na, 3.38; Sb, 17.92; Mo 33.88. Found: C, 5.88; H, 2.66; N, 1.52; Na, 3.18; Sb, 18.12; Mo 34.06. IR (KBr pellet): 3434 (vs), 3040 (vs), 1670(s), 1484(s), 1403(s), 951(s), 925(vs), 899(sh), 817(w), 656(s), 476(w).

General procedure for the selective oxidation of sulfides

In a typical experiment, sulfides (1 mmol), H_2O_2 (30 wt.%, 3 mmol), and catalyst (5 µmol) were added into a 50 mL roundbottom tube equipped with a reflux condenser. The reaction mixture was charged in the tube at the set temperature, and was stirred vigorously for 1 h. The resulting products were extracted with ethyl acetate, and analyzed by GC to determine the conversion and selectivity with n-dodecane as an internal standard.

X-ray crystallography

A crystal with dimensions $0.25 \times 0.18 \times 0.15$ mm³ for **1** was selected and stuck on a glass fiber. X-ray diffraction intensity data were recorded at 296 (2) K on a Bruker Apex-II CCD diffractometer with the graphite-monochromated Mo Ka radiation (λ = 0.71073 Å) (Table 2). Routine Lorentz and polarization corrections were applied, and a multi-scan absorption correction was performed using the SADABS program.¹⁶ Using Olex2,¹⁷ the structure was solved with the SHELXS-97¹⁸ structure solution program using Direct Methods and refined with the SHELXL¹⁹ refinement package using Least Squares minimisation. In the final refinement, the Sb, Mo, and Na atoms were refined anisotropically. No hydrogen atoms associated with the water molecules were located from the difference Fourier map. The lattice water molecules were determined by CHN element analysis and TGA results. All H atoms on water molecules were directly included in the molecular formula.

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Formula	$C_{16}H_{48}Mo_{12}N_4Na_5O_{66}Sb_5$		
M _r (g mol ⁻¹)	3227.56		
Crystal system	orthorhombic		
Space group	Cmcm		
a (Å)	12.2380(8)		
b (Å)	23.8258(16)		
C (Å)	13.8810(9)		
V (Å ³)	4047.4(5)		
Z	2		
Dc (g cm ⁻³)	2.648		
μ (mm ⁻¹)	3.564		
F (000)	3028.0		
20 range (deg)	3.742 to 50.194		
Reflections collected	10401		
Index ranges	-14 ≤ h ≤ 14, -28 ≤ k ≤ 25, -16 ≤ l ≤ 15		
Data/restraints/ parameters	1965/0/146		
GOF on F^2	1.087		
$R_{1,} w R_2 [I > 2\sigma (I)]$	$R_1 = 0.0517$, $wR_2 = 0.1422$		
R _{1,} wR ₂ [all data]	R ₁ = 0.0646, wR ₂ = 0.1536		

Results and discussion

Synthesis

As well known, Sb-containing POMs with unique structures and fascinating properties have been widely reported during the last decades. However, in contrast to the Sb-containing polyoxotungstates, their molybdate analogues are much less explored, especially for the Sb(V)-containing polyoxomolybdates. In this paper, an interesting Sb(V)containing Anderson-based cluster was synthesized using conventional aqueous method by reaction of Sb₂O₃, Sb₂O₅, (NH₄)₆Mo₇O₂₄·4H₂O and FeSO₄. It is noteworthy that relatively minor variations in reaction conditions can profoundly influence the identities of the products. (I) The reaction pH is a critical determinant in the syntheses of the crystals. Reasonable yields of crystalline products were obtained in the pH range of 5.2-5.6. Lower pH resulted in no products, while higher pH correlated with some amorphous precipitates. (II) Parallel experiments show that using NaOH solution to adjust pH value is especially important. Its presence is necessary to obtain pure bulk samples and no crystals suitable for singlecrystal X-ray diffraction could be obtained when NaOH solution was replaced by LiOH, KOH, or CsOH solution. (III) The presence of Sb_2O_3 and $FeSO_4$ is also crucial during the isolation of 1. Notably, although Sb₂O₃ and FeSO₄ were used as starting materials in the system, no Sb(III) and Fe ions were observed in the compound. Furthermore, no crystals were afforded when Sb^{3+} and Fe^{2+} were removed from the reaction. They may play a synergistic action with other materials in the reaction and the similar phenomena have been previously reported.²⁰



Fig. 1 (a) Polyanion structure of cluster **1** with thermal ellipsoids at the 50% probability level; (b) The ball-and-stick /polyhedral representation of polyoxoanion; (c) The space filling presentation of polyoxoanion. Color code: Sb, cyan; SbNa, turquoise; Mo, purple, O, red, Na, yellow; SbO₆, pink; MoO₆, blue.



Fig. 2 Packing of **1** in the solid state showing the porous coordination framework due to connection of the corners of the cluster anion by antimony/sodium-directed molecular assembly through oxo and hydroxo bridges. Color code: Sb, cyan; SbNa, turquoise; Mo, purple, O, red, Na, yellow. Hydrogen atoms are omitted for clarity.

Structural Descriptions

The molecular structure of compound **1** has been confirmed by single crystal X-ray diffraction. Compound 1 crystallizes in the orthorhombic system with space group Cmcm and consists of four TMA⁺ cations, five Na⁺ cations, eight protons, seventeen molecules and lattice water the polvoxoanion $[Na_5Sb_3(Sb_2Mo_{12}O_{57})]^{8-}$. And all the Sb and Mo atoms were sixcoordinated with octahedral geometry. It is noteworthy that there are serious crystallographic disorders in polyoxoanion. As shown in Fig. 1, the adjacent Anderson-type $\{SbMo_6\}$ units in 1 are linked alternatively via disordered Sb/Na and Na ions into a one-dimension (1D) chain. Interestingly, the adjacent {SbMo₆} units gave a mirror-symmetry representation as shown in Fig. S1. Additionally, 1 shows a porous solid-state framework, since the Anderson-based polyoxoanions further

250

Wavelength / nm

4 | J. Name., 2012, 00, 1-3



0 h

0.5 h 1 h

2 h 3 h

5 h

Wavelength / nm

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Fig. 3 XPS spectra of 1 for (a) Sb 3d3/2 and Sb 3d5/2; (b) Mo 3d3/2 and Sb 3d5/2.

form supramolecular coordination polymeric chains through the Sb/Na-O-directed molecular assembly in which the corners of the units are connected through Sb/Na oxo or hydroxo bridges (Fig. 2). Furthermore, considering the charge balance of compound 1, eight protons need to be added. The bond valence sum calculations of all the oxygen atoms in this compound indicate that all of these protons are delocalized, which is common in POM chemistry.²²

XPS Analyses and XRPD Patterns

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The bond valence sum (BVS) calculation of 1 manifests that the oxidation states of all Sb and Mo atoms are assigned to +5 and +6, respectively (Table S1).²² The XPS spectra of 1 were also recorded to further consolidate the chemical valences of Sb and Mo atoms (Fig. 3). The XPS spectrum of 1 for Sb atoms gives two peaks with binding energies (BEs) of 530.6 and 540.1 eV, attributed to Sb $3d_{5/2}$ and Sb $3d_{3/2}$ of the Sb (V) center (Fig. 3a). The Sb $3d_{5/2}$ and Sb $3d_{3/2}$ BE values in $\boldsymbol{1}$ are consistent with those [530.5 (Sb $3d_{5/2}$) and 540.1 eV (Sb $3d_{3/2}$)] observed in the pure Sb₂O₅ crystal.²³ Besides, the two apparent signals appearing at 236.2 and 235.7 eV are ascribed to Mo (VI) ions, respectively (Fig. 3b). The purity of the phases has been checked by comparison of the experimental X-ray powder pattern with the powder pattern calculated from the structure solved from single-crystal X-ray diffraction data (Fig. S5 in the ESI⁺). The differences in intensity between the experimental and simulated XPRD patterns might be due to the variation in preferred orientation of the powder sample during collection of the experimental XPRD.

UV spectra

The UV spectrum in aqueous solution in the region of 200-400 nm of 1 reveals two characteristic peaks (Fig. 4a), suggesting the presence of polyoxoanions.^{24a} The higher energy band at 206 nm is mainly anticipated due to the $p\pi$ -d π charge-transfer transition of the $O_t \rightarrow Mo$ bonds. Whereas, the lower energy absorption band at round 233 nm, can be attributed to the $p\pi\text{-}d\pi$ charge-transfer transitions of the $O_{b,c} \twoheadrightarrow$ Mo bonds. In order to investigate the stability of 1 in solution, in situ spectroscopic measurement was performed in the aqueous system (Fig. 4b). The unchanged position and strength of the absorption bands indicate that the aqueous system of 1 can stably exist at ambient temperature for at least 16 hours. As it is a well-known fact that POMs are pH sensitive and their stability is primarily depended on a particular reaction media, thus their studies are mainly specific and restricted on several

c) pH=4.6 pH=4.6 pH=5.2 pH=4.1 pH=6.3 pH=7.1 pH-3. pH=8. pH=2.8 pH=9.4 pH=2.3 pH=1.5 pH=10. pH=11.1 pH=11.7 pH=1.1 250 300 Wavelength / nm 300 350 Wavelength / nm Fig. 4 a) UV spectra of 1; b) The influence of time on the

b)

Absorbance

d)

stability of 1 in the aqueous solution; Influence of the pH values on the stability of 1 in aqueous solution: c) The UV spectral evolution in the acidic direction; d) The UV spectral evolution in the alkaline direction.

crucial parameters like solvents, concentration and pH value. To investigate the influence of pH on the stability of the compound in aqueous solution, compound 1 has been elaborately probed by means of UV spectra. In addition, the pH values in the acidic direction were adjusted using diluted HCl solution while the pH values in the alkaline direction were adjusted by using diluted NaOH solution. The initial pH value of **1** in water $(5 \times 10^{-5} \text{ mol L}^{-1})$ was 4.6. As is shown in Fig. 4c, the absorbance bands at 233 nm and 206 nm are gradually redshifted and become weaker and weaker at pH 3.7, which is a clear indication for the decomposition of the POM skeleton. The reason for the red-shift of the $O_t \rightarrow Mo$ band may be due to the protonation of the terminal oxygen atoms of polyoxoanions.^{24b} In contrast, from the aforementioned results, the UV spectra of 1 do not change at all even the pH value is increased to 10.6 (Fig. 4d). The above analyses show that compound 1 is quite stable in the broad pH range of 3.7-10.6 in aqueous solution.

FT-IR and TG analyses

The IR spectrum of 1 shows the skeletal vibrations in the region of $450-1000 \text{ cm}^{-1}$, which is in good agreement with the result of single-crystal X-ray structural analysis. The IR spectrum shows the O-H and N-H absorption bands as well as typical frequencies for Mo-O bands (Fig. S6). The characteristic absorptions of the polyanions below 1000 cm⁻¹ appear at ca. 951(s), 925(vs), 899(sh), 817(w), 656(s), 476(w). The signal appearing at 951 cm⁻¹ can be ascribed to the characteristic absorption of v(Mo-O_t). The characteristic peaks at 925, 899 and 817 cm⁻¹ are derived from the v(O_b–Mo–O_b) and v(Mo–O_c) vibrations.²⁵ And another peak at 656 cm⁻¹ is probably attributed to the absorptions of Sb-O stretching and bending vibrations.²

To investigate the thermal stability of 1, thermogravimetric analysis (TGA) was performed under a nitrogen flow as shown

in Fig. S7. The thermal decomposition process of **1** is defined in two steps. The first step corresponds to a weight loss of 9.34 % from 25 to 200 °C is mainly attributed to seventeen lattice water molecules (calcd 9.01 %). Subsequently, the rest of the observed weight loss (42.08 %) in the range of 200–900 °C, mainly due to the removal of eight protons (in the form of constitutional water moleculars), four TMA⁺ cations and the partial sublimation of MoO₃.

Catalytic Oxidation

Optimization of the catalyst

Based on literature investigation, Mo based catalysts are active and selective in sulfoxidation of thioethers.^{27a,b} Moreover, Mo-Sb oxides catalysts can also show high activities with good stabilities in sulfoxidation of two different thioethers, reported by Pârvulescu et al.^{27c,d} In view of this, the catalytic performance of catalyst 1 was evaluated in the oxidation of various sulfides by H₂O₂ under homogeneous conditions at 25°C. The effects of several reaction parameters on the oxidation reaction were studied in detail. To begin with, thioanisole, 1a was chosen as a model substrate for catalytic sulfoxidation reactions (Table 3). It is observed that the reaction is almost not feasible in the absence of the catalyst 1 (Table 3, entry 1). For the sake of comparison, we also envisaged antimony trioxide, antimony pentoxide and (NH₄)₆Mo₇O₂₄·4H₂O independently as a catalyst for the oxidation of thioanisoles and found them to be less active catalysts compared to 1 (Table S3). As seen in Fig. S8, the POM compounds will convert to the active polyoxoperoxo species in the presence of H_2O_2 and then sulfur-containing substrates were oxidized to the corresponding sulfoxides and sulfones. Next, we considered it imperative to examine the performance of the catalyst in a variety of solvents other than water, since solvents have been known to have immense influence on the activity and selectivity of catalyst in the sulfoxidation reaction.



Fig. 5 (a, b, c, d) Effect of catalyst amounts on the reaction of thioanisole (data were obtained by carrying out parallel experiments under the same experimental conditions).

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la	.s + H ₂ O ₂	Catalyst Solvent, RT		e^{0}_{s} +	
Entry	Catalyst (mol%)	Solvent	$H_2O_2^{\ b}$	Con. ^c (%)	Sel.(3a) (%)
1	_	H ₂ O		8.3	13.2
2	0.5	H₂O		100	100
3	0.5	CH₃CN		92	99
4	0.5	MeOH	3	85	>99
5	0.5	acetone		65	>99
6	0.5	CH_2CI_2		28	>99
7	0.25	H₂O		97	73
8	1.0	H₂O		100	>99
9	0.5	H₂O	1	38	97
10	0.5	H₂O	2	88	98
11	0.5	H₂O	4	100	100
12	0.5	H₂O	5	100	100
13 ^d	0.5	H₂O		100	100
14 ^e	0.5	H₂O	3	100	100
15 ^f	0.5	H ₂ O		94	98
12	0.5	п ₂ 0		94	98

^a Reaction conditions: substrate (1 mmol), catalyst 1, solvent (2 mL), 1 h, 25
^cC. Unless otherwise noted. ^b H₂O₂/substrate ratio. ^c Determined by GC analyses based on initial substrate. ^d 35 °C. ^e 45 °C. ^f Conversion and selectivity of the 11th cycle in the recycling studies.

Investigation of the solvents effect on 1a by using catalyst 1 showed that conversions of 92%, 85%, 65%, 28% in acetonitrile, methanol, acetone and dichloromethane, respectively, could be obtained (entries 3-6). The conversion of 1a reached 85% in a high protic solvent i.e using methanol (entry 4). It was found that acetone, an aprotic solvent, proved to be inefficient corresponding to its 65% conversion (entry 5). Additionally, the use of a less-polar solvent toluene afforded the phenyl methyl sulfone in the lowest conversion (entry 6). Surprisingly, strong proton donating solvent, water, not only exhibited its inherently greener characteristics compared to common organic solvents but also showed excellent conversion and selectivity. Henceforth, the oxidation of 1a was performed in water after much experimentation on optimizing solvent. In addition, the effect of catalyst dosage is also very important in the reaction optimization process because the concentration of the catalytically active species increased with higher catalyst dosage.²⁸ Fig. 5a illustrates the kinetic profile of the oxidation of thioanisole with different catalyst dosages under otherwise identical conditions. Noting that conversion of 1a gradually increases as the catalyst dosage is increased from 0.25 mol% to 1 mol% (entries 2, 7-8). In addition, the reaction time for a complete conversion can be shortened to 30 minutes with 1 mol% catalyst amount (Fig. 5a). Catalyst 1 with 0.25 mol% loading led to a low selectivity of 73% of corresponding sulfone (entry 7) (Fig. 5b). However, catalyst 1 exhibited a higher selectivity of 3a with increasing the catalyst amount (Fig. 5c, d). Therefore, the optimized catalyst dosage was proved to be 0.5 mol%, at which moderate conversion and excellent selectivity were achieved (entry 2).

DOI: 10.1039/C8DT01273C Journal Name

Table 4 Oxidation of various sulfides in water using H_2O_2 catalyzed by 1. ^a

Entry	Substrate	Time (h)	Product	Conv. b (%)	Sel. (%)
1	€ s ~	1		100	100
2	~ ^s ~⁄	0.8		100	100
3	~~s~~	3		100	100
4	~~~s~~~~	3		100	99
5		3		99	99
6	∫) ^s ∖	4		97	96
7	`s-{	4	o≈∭~_o∕	95	97
8		10		98	95
9		10		39	85
10 ^c		trace		-	-

^{*a*} Reaction conditions: sulfides (1 mmol), catalyst (0.5 mol%), H_2O (3 mL), 25 °C. Unless otherwise noted. ^{*b*} Determined by GC analyses based on initial substrate. ^{*c*} 50 °C.

As shown in Fig. S9, when the $H_2O_2/$ substrate (O/S) molar ratio was varied from 1:1 to 2:1 to 3:1 to 4:1 to 5:1, the degree of conversion ranged from 38%–88% to 100%–100%–100%, respectively (entries 2, 9–12). Based on these results, the O/S molar ratio of 3:1 was used for the following studies. Moreover, we have screened different temperatures for the oxidation of thioanisole. The conversions of **1a** at three different temperatures (25 °C, 35 °C and 40 °C) are a function of time (entries 2, 13–14). Obviously, there is an increase on the reaction rate with rising temperature (Fig. S10). However, from the view point of saving energy, we choose 25 °C for further investigation of the oxidation reaction of thioanisole. To confirm the recyclability of the homogeneous system, entry 2 worked as an example in the successive reactions. In the first run, the reaction converted 100% of **3a** in 1 h. Then the product was extracted with ethyl acetate and the catalyst existing in the aqueous medium was used for next catalytic run. The results (Fig. S11 in the ESI⁺) showed that the catalyst could be reused at least eleven times with a general decline (entry 15).

Sulfoxidation with different substrates

Having established the optimized reaction conditions for selective sulfoxidation of the model substrate, we extended the study to a range of structurally diverse sulfides and the results of which are summarised in Table 4. Under the optimized reaction conditions, both aryl and alkyl sulfides could be oxidized to the corresponding sulfones using 1 mmol of the substrate, 3 mmol of H_2O_2 and 5 μ mol of catalyst at 25 °C in H₂O. Ethyl methyl sulfide (entry 2) exhibited the highest activity among the sulfides surveyed. When dipropyl sulfides were used as substrates, the catalyst 1 exhibited excellent catalytic performance on prolonged reaction time of 3 hours (entry 3). Furthermore, the dibutyl sulfide was efficiently converted to the corresponding sulfone with 100% conversion and 99% selectivity over a further 3 h (entry 4). It is worth noting that some aryl sulfides could also be converted into the corresponding sulfones in high conversions and selectivities (entries 5-7). On the other hand, the steric hindrance effect of aryl-aryl thioethers appears to be the main factor affecting the yield of oxygenated products. On increasing the reaction temperature to 50 °C, phenyl sulfide (entry 8) was confirmed as a less-reactive substrate, with 98% over a further 10 h. The reaction system resulted in a dibenzothiophene (entry 9) of 39% conversion and 85% selectivity. In the case of 4,6dimethyldibenzothiophene (entry 10), significantly sluggish reactivity was detected after 10 hours. We could say that the present catalytic system could be applied to catalyze a wide range of sulfides.

Conclusions

In summary, a Sb-containing polyoxomolybdate cluster has been synthesized and characterized. Selective oxidation of various sulfides to the corresponding sulfones by using **1** as a homogeneous catalyst was demonstrated in the presence of H_2O_2 under mild conditions with excellent conversions and selectivity. Additionally, this homogeneous catalytic system not only catalyzed the oxidation of thioanisole with 100% conversion and 100% selectivity, but also could be reused in successive reactions with retention of the catalytic performance. Our further research will be focus on exploring the synthesis of novel structural analogues and their interesting catalytic properties.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful to the National Science Foundation of China (), the Foundation of Education Department of Henan Province ().

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View Article Online DOI: 10.1039/C8DT01273C Journal Name

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