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Copper(II)-containing tungstotellurates(VI): syntheses, structures and their catalytic performances in selective oxidation of thioethers†

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We report the syntheses and structures of two new copper(II)-containing tungstotellurates(VI) $Na_{12}[Te^{VI}_2W_8O_{38}Cu_2(H_2O)_2]\cdot7H_2O$ (**Te₂W₈Cu₂**) and $Na_6[Te^{VI}W_6O_{24}Cu(NH_2CH_2CO_2)_2]\cdot6H_2O$ (**TeW₆Cu**). The two compounds were synthesized by a simple one-pot method and characterized by single-crystal X-ray diffraction (XRD), powder XRD, FT-IR spectroscopy, elemental analysis, and thermogravimetric analysis in the solid state. Furthermore, their catalytic properties for the selective oxidation of thioethers were also studied systematically. The catalytic experiment results indicate that the tungstotellurate(VI) **Te₂W₈Cu₂** is an effective heterogeneous catalyst for the selective oxidation of thioethers to sulfoxides or sulfones by an H_2O_2 oxidant at room temperature. Under the ambient conditions, **Te₂W₈Cu₂** can convert 99% of methyl(phenyl)sulfane to sulfoxides or sulfones with 96% or 99% selectivity, respectively, and the utilization rate of H_2O_2 is up to 80%. Furthermore, **Te₂W₈Cu₂** as a heterogeneous catalyst is stable in the reaction and could be reused at least five cycles with conserved activity.

Introduction

The selective oxidation of thioethers into the corresponding sulfoxides is a very important process in organic synthesis chemistry, because the sulfoxides are a type of essential building block in pharmaceuticals, agrochemicals, and other fine chemicals.[1] Many significant methods have been developed for the synthesis of sulfoxides.[2,3] Traditionally, the process was carried out with a wide variety of oxidant agents, such as per-acids, dioxiranes, $NaIO_4$, MnO_2, CrO_3, SeO_2, and PhIO.[4] However, these oxidation reactions relied upon strong or environmentally-unfriendly oxidants, some of which are hazardous or toxic. Therefore, developing an environmentally benign method and using easily available oxidants in thioethers oxidation is attractive and needs to be further explored. H_2O_2 can be used as oxidant in the oxidation of thioethers because it's a green oxidant and water is the only by-product.[5] However, how to improve the utilization ratio and reduce the consumption of H_2O_2 with good catalytic selectivity in the oxidation reaction of thioethers still remains a challenge. In recent years, some

polyoxometalates (POMs) were used as effective catalysts for the oxidation of thioethers using H_2O_2 as oxidant.[6-8] In those re-ported procedures, low conversion of thioethers and the service life and reusability of the POM catalysts also need to be further improved. Consequently, based on the above reported results and our previous work on the oxidation of sulphides,[9] We believe that more attractive catalytic systems can be developed along this line to further increase the utility of these thioethers oxidation reactions by using some new stable and recyclable POM catalysts.

As we all know, POMs are a large class of discrete anionic metal–oxygen clusters of early transition metals with high oxidation states, such as Mo, W, V, Nb, Ta,[10-13] which present abundant structural diversity, favourable electrical carrier properties and great potentials in medicine, catalysis and material science.[14] The most significant subset of POMs is the heteropolyoxometalates that incorporate various anion templates as heterogroups, such as pyramidal groups ($\{Sb^{IV}O_3\}$, $\{Bi^{III}O_3\}$, $\{Se^{IV}O_3\}$), tetrahedral groups ($\{P^VO_4\}$, $\{Si^{IV}O_4\}$, $\{Ge^{IV}O_4\}$, $\{As^VO_4\}$), and octahedral groups ($\{I^{VI}O_6\}$, $\{Cr^{VI}O_6\}$, $\{Te^{VI}O_6\}$) *et al.*[15-17] It is well-known that the heterogroups play a key role in the structures and properties of these POMs, especially the redox properties, which is very important to their redox catalytic activities.[18] Since heteropolytungstates are usually synthesized in acidic media by the condensation of molybdate or tungstate with relevant heteroanions,[19] great achievements have been made for Keggin and Dawson type POMs by incorporating different tetrahedral heterogroups into their anionic cluster structures.[20] It is worth mentioning that the POMs with octahedral hererogroups usually present

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interesting redox properties and very few POMs with octahedral heterogroups were reported, especially with the $[Te^{VI}O_6]^{6-}$ heterogroup.[21] To the best of our knowledge, many Anderson–Evans type $[TeW_6O_{24}]^{6-}$ POM derivatives were reported such as $\{[Ni(H_2O)_3]_2[TeW_6O_{24}]\}$,[21] $\{[Ca(H_2O)_4]_2(TeW_6O_{24})\}^{2-}$[22] and $[4\text{-}H_2\text{-}methyl\text{-}imz]_6[TeW_6O_{24}]\cdot Te(OH)_6$.[23] In 2010, Ali and coauthors employed Anderson–Evans type POM $\{[Cu(en)_2]_3[TeW_6O_{24}]\}$ as catalyst for the epoxidation of cyclohexene and styrene showed good catalytic efficiency.[24] Recently, we reported the self-assembly of a series Ln(III)-containing tungstotellurates(VI) with interesting photoluminescence properties.[25]

In order to develop new stable and recyclable POM catalysts for selective oxidation of thioethers, in this work, we prepared two new copper(II)-containing tungstotellurates(VI) by a simple one-pot synthetic method. The two tungstotellurates(VI) $Na_{12}[Te_2^{VI}W_8O_{38}Cu_2(H_2O)_2]\cdot 7H_2O$ ($\textbf{Te}_2\textbf{W}_8\textbf{Cu}_2$) and $Na_6[Te^{VI}W_6O_{24}Cu(NH_2CH_2CO_2)_2]\cdot 6H_2O$ ($\textbf{TeW}_6\textbf{Cu}$) were fully characterized in solid state and their heterogeneous catalytic performances in selective oxidation of thioethers were also studied systematically in the presence of 30% H_2O_2.

Experimental

Materials and methods

$Na_6TeW_6O_{24}\cdot 22H_2O$ ($\textbf{TeW}_6$) was prepared according to the published procedure and characterized by IR spectroscopy.[26] All reagents were purchased from commercial sources, and used without further purification. Elemental analyses were determined by inductively coupled plasma mass spectrometry (ICP-MS) with PerkinElmer NexlON 350X spectrometer and the Elemental Analyser (C, H, N). FT-IR spectra (KBr pellets) were recorded with a Nicolet 170SX-FT/IR spectrometer. Thermogravimetric analyses were carried out with a TG-DTA 6200 device at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 instrument equipped with graphite-monochromatized Cu Kα radiation ($\lambda = 0.154060$ nm; scan speed = 8° min^{-1}; $2\theta = 5$–50°) at room temperature.

Synthetic procedures

Synthesis of $Na_{12}[Te_2^{VI}W_8O_{38}Cu_2(H_2O)_2]\cdot nH_2O$ ($n = 7$–38). A mixture of $Na_2WO_4\cdot 2H_2O$ (1.5 g, 4.55 mmol), $Te(OH)_6$ (0.1 g, 0.44 mmol), dimethylamine hydrochloride (1.5 g, 0.26 mmol), glycine (0.025 g, 0.05 mmol), $Cu(OAc)_2\cdot H_2O$ (0.075 g, 0.02 mmol) were dissolved in water (20 ml). The suspended solution was stirred for 2 hours. After filtration, the blue solution was kept in open air for slow evaporation, pH value of the solution is 8.9. The green crystals obtained after 1 week at room temperature (yield: 47% based on Te). Selected IR (2% KBr pellet, ν/cm^{-1}): 1631(m), 940(m), 884(s), 871(m), 689(m), 615(w), elemental analysis (%) for $Na_{12}[Te_2W_8O_{38}Cu_2(H_2O)_2]\cdot 7H_2O$: calcd Na 9.52, W 50.73, Te 8.80, Cu 4.38; found Na 8.80, W 51.50, Te 8.89, Cu 4.70.

Synthesis of $Na_6[Te^{VI}W_6O_{24}Cu(NH_2CH_2CO_2)_2]\cdot nH_2O$ ($n = 6$–20). The synthetic procedure is exactly extending process of that of $\textbf{Te}_2\textbf{W}_8\textbf{Cu}_2$. After removal of the green crystals of $\textbf{Te}_2\textbf{W}_8\textbf{Cu}_2$

following the above procedure, led to blue crystals of $\textbf{TeW}_6\textbf{Cu}$ within 2–3 days (yield: 21% based on Te). Selected IR (2% KBr pellet, ν/cm^{-1}): 1647(m), 1604(m), 1436(s), 1389(s), 1373(m), 1210(m), 1165(m), 1067(m), 959(m), 928(m), 903(w), 895(w), 699(m), 637(m), 551(m), 460(m), elemental analysis (%) for $Na_6[TeW_6O_{24}Cu(NH_2CH_2CO_2)_2]\cdot 6H_2O$: calcd. C 2.32, N 1.352, Na 6.66, W 53.2, Te 6.16, Cu 3.07; found C 2.32, N 1.608, Na 7.15, W 53.1, Te 6.38, Cu 3.07.

X-ray crystallography

Crystal data for all compounds were collected at 150 K on a Bruker APEX 2 DUO CCD single-crystal diffractometer equipped with a sealed Mo tube and a graphite monochromator ($\lambda = 0.71073$ Å). The selected crystals were selected by examination under mineral oil using a polarising microscope and mounted in a Hampton cryoloop with oil and placed within one minute under a stream of cold N_2. The structure solution and refinement were carried out by the *SHELXTL* program package (Bruker), and all structures were solved by direct methods and refined by the full-matrix least-squares method ($\Sigma w(|F_o|^2 - |F_c|^2)^2$).[27] The hydrogen atoms of waters were not incorporated in the refinements, and all other atoms were refined with anisotropic thermal parameters. The crystal data and structure refinement details for the two compounds are discussed and summarized in Table S1.† The crystallographic data have been deposited to the Cambridge Crystallographic Data Centre (CCDC) as entries CCDC-1991106, CCDC-1991107.

Catalytic oxidation of thioethers

The selective oxidation of thioethers using different catalysts were carried out as follows. Thioethers (0.5 mmol) and 30% H_2O_2 (0.6 mmol or 1.25 mmol) were dissolved in EtOH/MeCN (1 ml) in a pressure tube (10 ml), then added catalyst (0.17 mol%) with a sealing cap at room atmosphere. The reaction mixture was vigorously stirred until the completion as indicated by GC. The reaction mixture was filtered through a short pad of celite and quenched with water. Then the mixture was extracted with dichloromethane (10 ml × 3), dried over $MgSO_4$, and evaporated under reduced pressure to afford the crude product, which was further purified by flash chromatography on silica gel with *n*-hexane/EtOAc to obtain the corresponding sulfoxides or sulfones. In the recycle experiments, the catalyst was filtered after the reaction and washed with dichloromethane and dried under vacuum at 50 °C and used for the next cycle.

Results and discussion

Synthesis and structure description

As described in the synthetic procedures above, the two copper(II)-containing tungstotellurates(VI) $\textbf{Te}_2\textbf{W}_8\textbf{Cu}_2$ and $\textbf{TeW}_6\textbf{Cu}$ were prepared by simple one-pot reaction with a time-resolved process in which the hydrated salts of the two compounds were isolated successively from the same mother liquor as bulk-pure materials. The crystals of $\textbf{Te}_2\textbf{W}_8\textbf{Cu}_2$ were isolated firstly and then the crystals of $\textbf{TeW}_6\textbf{Cu}$. We noticed that the glycine

ligand plays a very important role in the synthesis of the two compounds although it is absent in the final structure of **Te$_2$W$_8$Cu$_2$**. Moreover, heteropolytungstates are usually formed in condensation reactions of tungstate oxoanions with relevant heteroanions in an acid medium, but the two copper(II)-containing tungstotellurates(VI) were obtained straightly in the reaction solution without addition of appropriate acid and the pH value is 8.9, which means the two compounds can be constructed in the presence of Te(OH)$_6$ which can provide enough protons during the condensation reactions.

Single-crystal X-ray diffraction analysis reveals that **Te$_2$W$_8$Cu$_2$** is a di-copper-containing tungstotellurate(VI) which crystallizes in the triclinic lattice with space group $P\bar{1}$. As shown in Fig. 1a, the polyanion cluster $[Te^{VI}_2W_8O_{38}Cu_2(H_2O)_2]^{12-}$ comprises two {TeW$_4$O$_{19}$} subunits linked *via* two five-coordinate Cu^{II} ions in an anti-conformation. The {TeW$_4$O$_{19}$} subunit is a divacant fragment of the well-known Anderson–Evans structure {TeW$_6$O$_{24}$}, in which four edge-sharing WO$_6$ octahedron formed a slightly distorted di-vacant hexagon and the central octahedral cavity is occupied by a {Te^{VI}O$_6$} heterogroup. The Te–O bond length are in the range of 1.881(4) Å to 1.968(4) Å, and the average distance is 1.928(4) Å. The two {TeW$_4$O$_{19}$} subunits are further connected by two Cu^{II} ions *via* multiple W–O–Cu and Te–O–Cu bonds. Each Cu^{II} center adopts a distorted square-pyramidal coordination sphere which tetra-coordinated by four terminal O atoms in the square plane from two {TeW$_4$O$_{19}$} subunits, and the Cu–O bond length is between 2.092(2) to 2.108(2) Å, which is comparable to the Cu–O bond lengths reported. The last coordinate site of Cu^{II} center is occupied by one terminal H$_2$O at the conic node position of the square-pyramidal. The two Cu^{II} ions are not within the same planar of {TeW$_4$O$_{19}$} subunits and connected *via* two μ_3-O atoms from the {TeO$_6$} heterogroups, the distance between the two Cu^{II} ions is 3.031(1) Å and the angle of Te–O–Cu is averaging 126.2°, the other bond lengths and angles are summarized in Table S2.† The individual $[Te^{VI}_2W_8O_{38}Cu_2(H_2O)_2]^{12-}$ polyanions can be further linked by sodium ions to form a 3D structure in solid state, as shown in Fig. S1a.†

For compound **TeW$_6$Cu**, X-ray diffraction analysis reveals that it consists of one dimensional organic–inorganic hybrid polymeric chains having zig–zag architecture, which crystallizes in the triclinic lattice with space group $P\bar{1}$ in form of sodium salts. As shown in Fig. 1b, the polymeric chain is formed by Anderson–Evans type $[Te^{VI}W_6O_{24}]^{6-}$ polyoxoanion and {Cu(gly)$_2$} complex *via* the multiple O–Cu–O bonds. The polyoxoanion $[Te^{VI}W_6O_{24}]^{6-}$ in **TeW$_6$Cu** is similar to the structures reported for other Anderson–Evans type anions with D_{3d} symmetry, in which a {TeO$_6$} octahedron is surrounded by six edge-sharing {WO$_6$} octahedra. The Te–O bond distances and O–Te–O bond angles are exhibited in Table S2,† and it can conclude that there is only mild distortion of the {Te^{VI}O$_6$} octahedra. The Cu^{II} centers in the chain present a distorted octahedral coordination sphere which is tetra-coordinated by two O atoms and two N atoms positioned in the equatorial plane from the carboxylate and amine groups of two glycine ligands, and the other two coordinate sites at the apical position are occupied by two O atoms from the neighbouring $[Te^{VI}W_6-O_{24}]^{6-}$ polyoxoanions. The individual polymeric chains can be further linked by sodium ions to form a 3D structure in solid state, as shown in Fig. S1b.†

Catalysis

Selective oxidation of thioethers to the versatile utility of sulfoxides and sulfones is considered to be a topical interest in organic synthesis. As mentioned above, POMs can be used as effective catalysts for the oxidation of thioethers using H$_2$O$_2$ as oxidant. In this work, in order to further develop a more attractive catalytic system for the selective oxidation of thioethers, we selected three different tungstotellurates(VI), the classic Anderson–Evans type POM **TeW$_6$**, the organic–inorganic hybrid complex **TeW$_6$Cu**, and the di-copper-containing POM **Te$_2$W$_8$Cu$_2$**, as heterogeneous catalysts for this reaction and optimized the reaction conditions systematically. Moreover, we also verified that the **Te$_2$W$_8$Cu$_2$** is an effective heterogeneous catalyst with good conversion and selectivity for the oxidation of different thioethers to corresponding sulfoxides or sulfones at room temperature.

In order to investigate the catalytic performance and effects of the different catalysts for selective oxidation of thioethers, **Te$_2$W$_8$Cu$_2$**, **TeW$_6$Cu**, **TeW$_6$**, CuO and Cu(OAc)$_2$ were used as catalysts, and the catalytic reaction experiments of the oxidation of thioethers were investigated systematically by using H$_2$O$_2$ as oxidant under different conditions. At the beginning of our studies, in order to find out the best catalyst and optimize the reaction conditions for this catalytic system, methyl phenyl sulfide (**1a**) was employed as the model substrate for the oxidation reaction. The catalytic study results were summarized in Table 1. Notably, when the reaction was carried out in the absence of catalysts, only trace of product methyl phenyl sulfoxide (**2a**) was observed, and no methyl phenyl sulfone (**3a**) was observed, and the intact substrate **1a** can be recovered (Table 1, entry 1). The copper(II) salts and oxides, such as Cu(OAc)$_2$ and CuO were first evaluated in the reaction (**1a** to **2a**), although the selectivity of **2a** was 99%, while the conversion of **1a** were 19%

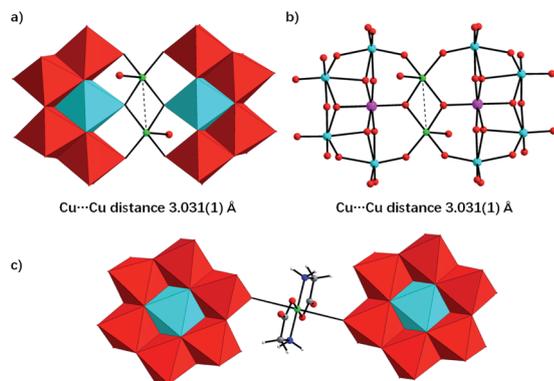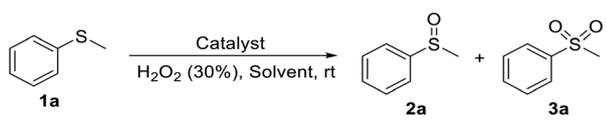**Fig. 1** Polyhedral/ball-and-stick representation of the core structures of **Te$_2$W$_8$Cu$_2$** (a and b) and **TeW$_6$Cu** (c). Color code: WO$_6$, red octahedron; TeO$_6$, turquoise octahedron, Cu, green balls, O, red balls, C, light gray balls, N, blue balls, H, white balls.

Table 1 Optimization of reaction conditions[a]

Entry	Catalyst	Conv.[b] (%)	2a Sel.[b] (%)	3a Sel.[b] (%)	UR (%) (H$_2$O$_2$)
1[c]	None	3	99	0	2.5
2[c]	TeW$_6$Cu	89	86	14	64
3[c]	Te$_2$W$_8$Cu$_2$	99	96	4	80
4[d]	Te$_2$W$_8$Cu$_2$	91	96	4	73
5[e]	TeW$_6$Cu	99	7	93	74
6[e]	Te$_2$W$_8$Cu$_2$	99	1	99	79
7[f]	Te$_2$W$_8$Cu$_2$	99	21	79	79

[a] Reaction conditions: **1a** (0.5 mmol), catalyst (0.17 mol%), solvent (1 ml). [b] Yields determined by GC analysis using 1-adamantanol as an internal standard. [c] H$_2$O$_2$ (30%) (1.2 equiv.), MeOH or EtOH (1 ml), 8 h. [d] H$_2$O$_2$ (30%) (1.0 equiv.), MeOH or EtOH (1 ml), 8 h. [e] H$_2$O$_2$ (30%) (2.5 equiv.), MeCN (1 ml), 6 h. [f] H$_2$O$_2$ (30%) (2.0 equiv.), MeCN (1 ml), 8 h. UR = utilization rate.

and 31%, respectively. Considering the Anderson–Evans type **TeW$_6$** is the basic structure of **TeW$_6$Cu**, we also tested the activity of **TeW$_6$** in the model reaction (**1a** to **2a**). The results show that the conversion of **1a** was 88% and the selectivity of **2a** was 84%. Continuing experiments, the activity of **TeW$_6$Cu** and **Te$_2$W$_8$Cu$_2$** were also examined in the model reaction, as shown in Table 1. Interestingly, according to the results of the catalysts screening, the final conversion of **1a** and selectivity of **2a** and **3a** indicate that **Te$_2$W$_8$Cu$_2$** is the best catalyst for the both selective oxidation reactions of **1a** to **2a** and **1a** to **3a** (Table 1, entries 1–7) under ambient conditions. The selectivity of **2a** is up to 96% when using MeOH or EtOH as solvent (Table 1, entry 3). Compared to 1.0 equiv. H$_2$O$_2$ (30%), the 1.2 equiv. H$_2$O$_2$ (30%) showed almost equal quality conversion rate (99%) of **1a** (Table 1, entries 3–4). Furthermore, the selectivity of **3a** is up to 99% when using MeCN as solvent and H$_2$O$_2$ (30%) (2.5 equiv.) as oxidant (Table 1, entry 6), which is much better than using H$_2$O$_2$ (30%) (2.0 equiv.) as oxidant. Based on the results summarized in Table 1, the optimized reaction conditions for this catalytic system are as follow: (**1a** to **2a**): 0.17 mol% **Te$_2$W$_8$Cu$_2$**, 1.2 equiv. of H$_2$O$_2$ (30%) in 1.0 ml of MeOH or EtOH at room temperature for 8 h; (**1a** to **3a**) 0.17 mol% **Te$_2$W$_8$Cu$_2$**, 2.5 equiv. of H$_2$O$_2$ (30%) in 1.0 ml of MeCN at room temperature for 6 h.

The variation of different catalysts **Te$_2$W$_8$Cu$_2$**, **TeW$_6$Cu**, **TeW$_6$**, CuO and Cu(OAc)$_2$ with reaction time in the oxidation reaction is demonstrated in Fig. 2a, and their kinetic studies indicated that if the reaction was carried out using **Te$_2$W$_8$Cu$_2$** as catalyst, the reaction proceeded much faster than using other catalysts, which means the **Te$_2$W$_8$Cu$_2$** present best activity for this reaction. The initial velocity order of the different catalysts is **Te$_2$W$_8$Cu$_2$** > **TeW$_6$Cu** > **TeW$_6$** > CuO > Cu(OAc)$_2$ > no catalyst (41.70 > 23.18 > 18.88 > 17.50 > 6.79 > 1.17, conversion moles per unit time). There are two possible reasons may explain these
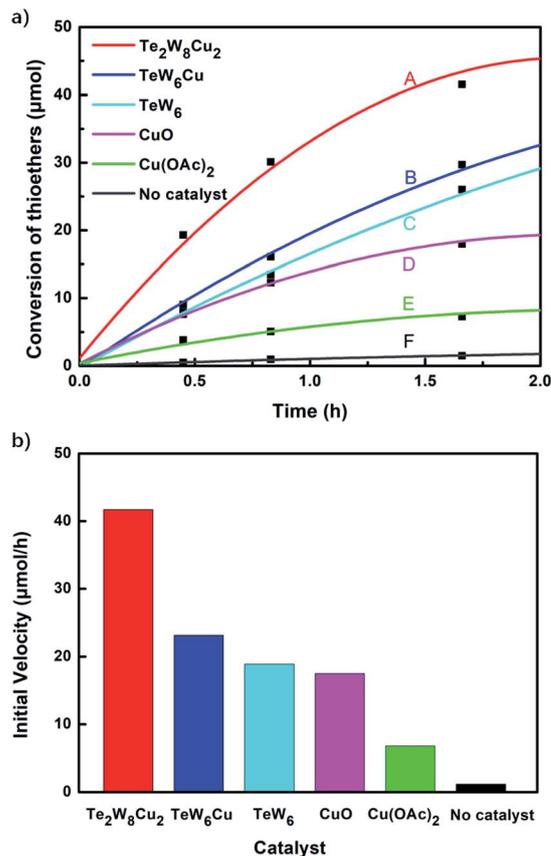

Fig. 2 The conversion of thioanisole **1a** with reaction time in the oxidation of thioanisole reaction by the catalyst of **Te$_2$W$_8$Cu$_2$**, **TeW$_6$Cu**, **TeW$_6$**, CuO and Cu(OAc)$_2$ (a). The initial velocity of the reaction by using different catalysts (b). (Reaction conditions: thioanisole **1a** (0.5 mmol), catalyst (0.17 mol%), 30% H$_2$O$_2$ (1.0 equiv.), EtOH (1 ml), rt. All catalyst has the same number of moles of Cu, except **TeW$_6$**. 1-adamantanol as an internal standard).

results. Firstly, many other POMs were used as effective catalyst for the oxidation of thioethers due to their excellent redox properties, and the tungstotellurates(VI) **Te$_2$W$_8$Cu$_2$**, **TeW$_6$Cu**, **TeW$_6$** with {Te^{VI}O$_6$} heterogroup can also present interesting oxidation catalytic activity which is much better than the simple cupric salts and cupric oxides for the selective oxidation of thioethers. Sencondly, by introducing the Cu^{II} ions into the structures of the tungstotellurates(VI) **Te$_2$W$_8$Cu$_2$** and **TeW$_6$Cu**, the Cu^{II}-containing tungstotellurates(VI) are more active than the simple Anderson–Evans type tungstotellurates(VI) **TeW$_6$**, because the Cu^{II} centers can affect their redox properties and offer the new active sites for the catalysts during the catalytic reaction. More importantly, the structure and the coordination environment of Cu^{II} in **Te$_2$W$_8$Cu$_2$** and **TeW$_6$Cu** are different, which can also affect their catalytic activity for selective oxidation of thioethers. As proved by single crystal analyses, for **Te$_2$W$_8$Cu$_2$**, there are two Cu^{II} centers in the structure, and each Cu^{II} center is five-coordinated square-pyramidal coordination sphere, which make it beneficial to active the substrates (sulfide and H$_2$O$_2$). While in **TeW$_6$Cu**, the Cu^{II} center is six-coordinated with an octahedra coordination sphere, and the Cu^{II} center is

coordination-saturated, resulting in strong coordination of the ligand to Cu. The results make the Cu^{II} in **TeW$_6$Cu** is less active to the substrates. So the activity of **Te$_2$W$_8$Cu$_2$** is higher than **TeW$_6$Cu**. Based on the above results, **Te$_2$W$_8$Cu$_2$** can be proved as the best optimal catalyst for the oxidation reaction under this conditions. Moreover, the heterogeneous nature of **Te$_2$W$_8$Cu$_2$** was also investigated by a leaching experiment. As shown in Fig. 3, when the conversion of **1a** reached to about 38% at 0.5 h, the catalyst was filtered off and the filtrate continued to react under the same conditions for 6 h, the reaction almost stopped and the conversion of **1a** increased slightly due to the transformation of **1a** itself without catalyst under such reaction conditions. The result revealed that the catalyst of **Te$_2$W$_8$Cu$_2$** is a heterogeneous catalyst in this reaction and stable without leaching under the optimized conditions.

As far as we know, the mechanism of catalytic oxidation reaction using H$_2$O$_2$ as oxidant usually shows two different pathways, the radical pathway and the peroxo species pathways. To further understand the mechanism of our system, the oxidation of thioethers using H$_2$O$_2$ as oxidant and **Te$_2$W$_8$Cu$_2$** as catalyst, radical trap experiments on the oxidation of methyl(phenyl)sulfane were employed (ESI, Table S3†). The reaction was carried out under the optimized conditions, after adding Ph$_2$NH as oxygen-radical scavenger, 1,4-benzoquinone as superoxide ($^\cdot$O^{2-}/$^\cdot$O$_2$H scavenger) and *tert*-butyl alcohol as a hydroxyl radical scavenger,[28] no obvious changes on the conversion and selectivity were observed (ESI, Table S3†). The results indicate that the mechanism of the reaction is not a radical pathway, which is consistent with previous literature that POMs tend to form peroxo-metal species in the presence of H$_2$O$_2$.[29] So, we proposed that an active peroxo species formed during the reaction by using H$_2$O$_2$ as oxidant and **Te$_2$W$_8$Cu$_2$** as catalyst, although it has not been tested in this work.

According to the study of the catalytic performance of different catalysts for selective oxidation of thioethers, we noticed that the tungstotellurates(VI) **Te$_2$W$_8$Cu$_2$**, **TeW$_6$Cu** and **TeW$_6$** shown good catalytic potentials for this system, we think the {Te^{VI}O$_6$} heterogroup may sufficiently affect the redox property of the tungstotellurate(VI) catalysts which might be good for their catalytic activity of selective oxidation
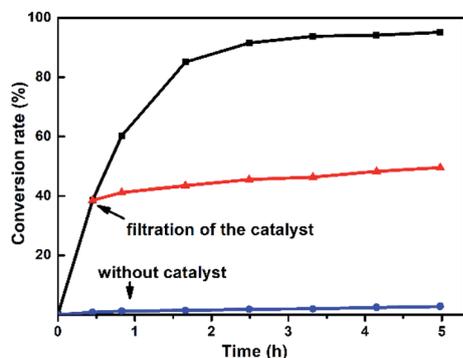
of thioethers. Moreover, the copper-containing tungstotellurates(VI) **Te$_2$W$_8$Cu$_2$** and **TeW$_6$Cu** present better catalytic activity than the classic Anderson–Evans type tungstotellurates(VI) **TeW$_6$**, which means introducing Cu^{II} centers in to the POM based complexes can improve the catalytic activity of tungstotellurates(VI), especially the **Te$_2$W$_8$Cu$_2$** with two Cu^{II} centers. Because the heterogeneous catalyst **Te$_2$W$_8$Cu$_2$** shows best catalytic activities for the selective oxidation of thioethers (Table 1), we studied systematically the catalytic performance of selective oxidation of different thioethers to corresponding sulfoxides using H$_2$O$_2$ (30%) (1.2 equiv.) as oxidant. A variety of organic sulfur compounds were subjected to this highly chemoselective catalytic system. As shown in Table 2, all of the desired sulfoxides products were obtained in moderate to good yield. Surprisingly, electron-donating as well as electron-withdrawing substituted phenyl ring thioanisole gave the desired sulfoxides (**2a**–**2f**) in high yields with good selectivities and high H$_2$O$_2$ utilization rate. Ethyl phenyl sulfide **1g** can be converted into ethyl phenyl sulfoxide **2g** with 99% conversion and 93% selectivity. The sterically more hindered substrate diphenylsulfane **1h** were also investigated in this catalytic system. Fortunately, the corresponding product **3h** was obtained in moderate yield. It is worth noting that less reactive dibutylsulfane **1i** could be efficiently oxidized into the desired sulfoxides **2i** in high yields with 98% selectivity.

Table 2 Selective oxidation of thioethers to sulfoxides^a

R—⟨⟩—S—R^1 **Te$_2$W$_8$Cu$_2$** (0.17 mol%) / H$_2$O$_2$ (30%), EtOH, rt → R—⟨⟩—S(=O)—R^1
1 → **2**

Entry	Substrate **1**	Conv.^{b} (%)	Product **2**	Sel^b. (%)	UR (%) (H$_2$O$_2$)
1	R = H	99	**2a**	96	80
2	R = Me	99	**2b**	95	79
3	R = MeO	99	**2c**	98	81
4^c	R = Ac	99	**2d**	91	75
5^c	R = Cl	99	**2e**	93	77
6^c	R = NO$_2$	95	**2f**	90	71
7	R^1 = Et	99	**2g**	93	77
8^d	R^1 = Ph	90	**2h**	66	54
9	R = R^1 = nBu	99	**2i**	98	81

^{a} Reaction conditions: **1** (0.5 mmol), catalyst **Te$_2$W$_8$Cu$_2$** (0.17 mol%), EtOH (1 ml), H$_2$O$_2$ (30%) (1.2 equiv.), 8 h. ^{b} Isolated yield. ^{c} 12 h. ^{d} 15 h.

Fig. 3 Leaching test for the oxidation of thioanisole **1a** to **2a** by using **Te$_2$W$_8$Cu$_2$** as catalyst. (Reaction conditions: **1a** (0.5 mmol) **Te$_2$W$_8$Cu$_2$** (0.17 mol%), 30% H$_2$O$_2$ (1.2 equiv.), EtOH (1.0 ml), rt).

Furthermore, we also explored its catalytic activity for selective oxidation of different thioethers to corresponding sulfones using H_2O_2 (30%) (2.5 equiv.). As shown in Table 3, a broad array of organic sulfur compounds worked well to afford the corresponding sulfones in good to excellent yields (Table 3, entries 1–9). It is worth noting that sterically hindered substrate diphenylsulfane **1h** and less reactive dibutylsulfane **1i** gave the corresponding sulfones **3h** and **3i** in 71% and 99% selectivity, respectively. Interestingly, we noticed that the molar ratio of H_2O_2 and **Te$_2$W$_8$Cu$_2$** plays a very important role for the selectivity of thioethers to corresponding sulfoxides and sulfones. This results are much better than other catalytic system using H_2O_2 as oxidant, and in this work we have developed a good method to improve the utilization ratio and reduce the consumption of H_2O_2 with good catalytic selectivity in the oxidation reaction of thioethers by using **Te$_2$W$_8$Cu$_2$** as catalyst. It is interesting to see that different oxidized products can be performed in high selectivity by using different solvents. The reason could be that the hydrogen bond and interaction between the reactants and solvents are different in ethanol and acetonitrile, which could solvate H_2O_2 effectively and thereby reduce its availability at the surface of catalyst.

As mentioned above, we have investigated the heterogeneous nature of **Te$_2$W$_8$Cu$_2$** by a leaching experiment, which reveals that the catalyst is a heterogeneous catalyst in this reaction and stable without leaching under the optimized
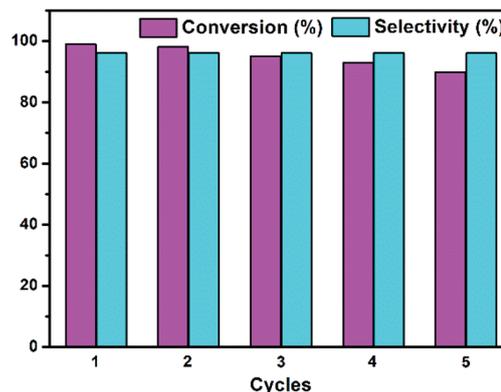

Fig. 4 Recycle test for the oxidation of thioanisole **1a** to **2a** by **Te$_2$W$_8$Cu$_2$**. (Reaction conditions: **1a** (0.5 mmol) **Te$_2$W$_8$Cu$_2$** (0.17 mol%), 30% H_2O_2 (1.2 equiv.), EtOH (1.0 ml) at rt.).

condition. Therefore, in order to the service life and reusability of the catalyst, we also evaluated the recyclability and stability of **Te$_2$W$_8$Cu$_2$** for the selective oxidation of thioethers. As shown in Fig. 4, the catalytic reactivity of **Te$_2$W$_8$Cu$_2$** remains without obviously decreasing the conversion and selectivity after 5 cycles, which means the catalyst is recyclable and reusable after the reaction. The results of comparison of FT-IR spectra of the catalyst before and after the recycle reactions also confirms that the structure of **Te$_2$W$_8$Cu$_2$** is stable without decomposition in the reaction (ESI, Fig. S5†). This results indicate that the structure of **Te$_2$W$_8$Cu$_2$** is very favourable for this catalytic system. The recyclability and stability of **TeW$_6$** and **TeW$_6$Cu** were also evaluated (ESI, Fig. S6 and S7†). Interestingly, the stability order of the catalyst is **Te$_2$W$_8$Cu$_2$** > **TeW$_6$Cu** > **TeW$_6$**. The results indicate that the new catalyst becomes more stable than POMs when the Cu^{II} centers were introduced into the POMs.

Conclusions

In summary, we have synthesized two new copper-containing tungstotellurates(VI) **Te$_2$W$_8$Cu$_2$** and **TeW$_6$Cu** by a simple one pot reaction which were characterized by single-crystal X-ray diffraction(XRD), powder XRD, FT-IR spectroscopy, elemental analysis, and thermogravimetric analysis in solid state. The catalytic properties of the tungstotellurates(VI) for the selective oxidation of thioethers were also studied systematically. The compound **Te$_2$W$_8$Cu$_2$** showed very high catalytic activity for the selective oxidation of thioethers to sulfoxides (conversion: up to 99%, selectivity: up to 98%) and sulfones (conversion: up to 99%, selectivity: up to 98%) by H_2O_2 under ambient conditions. In addition, the **Te$_2$W$_8$Cu$_2$** catalyst was stable in the environmentally benign catalytic system and could be reused at least five cycles without a significant loss of reactivity on the model reaction. This work offer a new strategy for the selective oxidation of thioethers by using tungstotellurates(VI) as heterogeneous catalyst, and the utilization ratio of the oxidant H_2O_2 is up to about 80%.

Table 3 Selective oxidation of thioethers to sulfones[a]

Entry	Substrate 1	Conv.[b] (%)	Product 3	Sel.[b] (%)	UR (%) (H_2O_2)
1	R = H	99	**3a**	99	79
2	R = Me	99	**3b**	99	79
3	R = MeO	99	**3c**	99	79
4[c]	R = Ac	99	**3d**	98	78
5[c]	R = Cl	99	**3e**	97	77
6[c]	R = NO$_2$	99	**3f**	96	77
7	R^1 = Et	99	**3g**	99	79
8	R^1 = Ph	96	**3h**	71	54
9[d]	R = R^1 = nBu	99	**3i**	99	79

[a] Reaction conditions: **1** (0.5 mmol), catalyst **Te$_2$W$_8$Cu$_2$** (0.17 mol%), MeCN (1 ml), H_2O_2 (30%) (2.5 equiv.), rt, 6 h. [b] Isolated yield. [c] 10 h. [d] 40 °C, 10 h.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 (a) M. C. Carreno, *Chem. Rev.*, 1995, **95**, 1717; (b) H. L. Holland, *Chem. Rev.*, 1988, **88**, 473.

2 (a) I. Fernaández and N. Khiar, *Chem. Rev.*, 2003, **103**, 3651; (b) S. Caron, R. W. Dugger, S. G. Ruggeri, J. A. Ragan and D. H. B. Ripin, *Chem. Rev.*, 2006, **106**, 2943.

3 (a) C. Bolm, *Coord. Chem. Rev.*, 2003, **237**, 245; (b) A. Rajendran, T. Cui, H. Fan, Z. Yang, J. Feng and W. Li, *J. Mater. Chem. A*, 2020, **8**, 2246.

4 (a) J.-E. Bäckvall, in *Modern Oxidation Methods*, ed. J.-E. Bäckvall, Wiley-VCH, Weinheim, 2004, p. 193; (b) K. Kaczorowska, Z. Kolarska, K. Mitka and P. Kowalski, *Tetrahedron*, 2005, **61**, 8315; (c) M. Yadav, A. Bhunia, S. K. Jana and P. W. Roesky, *Inorg. Chem.*, 2016, **55**, 2701.

5 (a) M. Liu, S. Shi, L. Zhao, M. Wang, G. Zhu, X. Zheng, J. Gao and J. Xu, *ACS Catal.*, 2018, **8**, 683; (b) M. Attoui, E. Pouget, R. Oda, D. Talaga, G. L. Bourdon, T. Buffeteau and S. Nlate, *Chem.–Eur. J.*, 2018, **24**, 11344; (c) P. Cruz, M. Fajardo, I. del Hierro and Y. Pérez, *Catal. Sci. Technol.*, 2019, **9**, 620.

6 L. Huang, S.-S. Wang, J.-W. Zhao, L. Cheng and G.-Y. Yang, *J. Am. Chem. Soc.*, 2014, **136**, 7637.

7 Y. Wang, X. Kong, W. Xu, F. Jiang, B. Li and L. Wu, *Inorg. Chem.*, 2018, **57**, 3731.

8 Z.-W. Cai, T. Yang, Y.-J. Qi, X.-X. Li and S.-T. Zheng, *Dalton Trans.*, 2017, **46**, 6848.

9 (a) J. K. Li, Y. Q. Xu and C. W. Hu, *Inorg. Chem. Commun.*, 2015, **60**, 12; (b) J.-K. Li, J. Dong, C.-P. Wei, S. Yang, Y.-N. Chi, Y.-Q. Xu and C.-W. Hu, *Inorg. Chem.*, 2017, **56**, 5748; (c) J. Dong, J. F. Hu, Y. N. Chi, Z. G. Lin, B. Zou, S. Yang, C. L. Hill and C. W. Hu, *Angew. Chem., Int. Ed.*, 2017, **56**, 4473; (d) J. Dong, H. J. Lv, X. R. Sun, Y. Wang, Y. M. Ni, B. Zou, N. Zhang, A. X. Yin, Y. N. Chi and C. W. Hu, *Chem.–Eur. J.*, 2018, **24**, 19208; (e) X. Sun, J. Dong, Z. Li, H. Liu, X. Jing, Y. Chi and C. Hu, *Dalton Trans.*, 2019, **48**, 5285.

10 P. A. Lorenzo-Luis, P. Gili, A. Sanchez, E. Rodriguez-Castellon, J. Jimenez-Jimenez, C. Ruiz-Perez and X. Solans, *Transition Met. Chem.*, 1999, **24**, 686.

11 J. Lu, X. Ma, P. Wang, J. Feng, P. Ma, J. Niu and J. Wang, *Dalton Trans.*, 2019, **48**, 628.

12 J. Liu, M. Jin, L. Chen and J. Zhao, *Inorg. Chem.*, 2018, **57**, 12509.

13 J. M. Cameron, J. Gao, D. Long and L. Cronin, *Inorg. Chem. Front.*, 2014, **1**, 178.

14 B. Artetxe, S. Reinoso, L. San Felices, P. Vitoria, A. Pache, J. Martin-Caballero and J. M. Gutierrez-Zorrilla, *Inorg. Chem.*, 2015, **54**, 241.

15 J. Gao, J. Yan, S. G. Mitchell, H. N. Miras, A. G. Boulay, D. Long and L. Cronin, *Chem. Sci.*, 2011, **2**, 1502.

16 Q. Han, J. Liu, Y. Wen, L. Chen, J. Zhao and G. Yang, *Inorg. Chem.*, 2017, **56**, 7257.

17 B. Kandasamy, B. S. Bassil, A. Haider, J. Beckmann, B. Chen, N. S. Dalal and U. Kortz, *J. Organomet. Chem.*, 2015, **796**, 33.

18 J. Kang, J. Ahn, H. Shin, S. Pyo, H. Yun and J. Do, *Z. Kristallogr.–New Cryst. Struct.*, 2011, **226**, 129.

19 E. M. Limanski, D. Drewes, E. Droste, R. Bohner and B. Krebs, *J. Mol. Struct.*, 2003, **656**, 17.

20 B. Kandasamy, B. S. Bassil, J. Beckmann, B. Chen, N. S. Dalal and U. Kortz, *J. Cluster Sci.*, 2017, **28**, 825.

21 B. Gao, S. Liu, C. Zhang, L. Xie, C. Sun and M. Yu, *J. Coord. Chem.*, 2007, **60**, 911.

22 K. Boubekeur, R. Riccardi, P. Batail and E. Canadell, *Comptes Rendus de l'Académie des Sciences–Series IIC*, 1998, **1**, 627.

23 P. A. Lorenzo-Luis, P. Gili, A. Sánchez, E. Rodriguez-Castellón, J. Jiménez-Jiménez, C. Ruiz-Pérez and X. Solans, *Transition Met. Chem.*, 1999, **24**, 686.

24 D. Dutta, A. D. Jana, M. Debnath, A. Bhaumik, J. Marek and M. Ali, *Dalton Trans.*, 2010, **39**, 11551.

25 S. Shang, Z. Lin, A. Yin, S. Yang, Y. Chi, Y. Wang, J. Dong, B. Liu, N. Zhen, C. L. Hill and C. Hu, *Inorg. Chem.*, 2018, **57**, 8831.

26 K. J. Schmidt, G. J. Schrobilgen and J. F. Sawyer, *Acta Crystallogr. Sect. C Cryst. Struct. Commun.*, 1986, **42**, 1115.

27 (a) G. M. Sheldrick, *SHELXL 97 Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997; (b) *SHELXTL v6.14*, Bruker Analytical X-ray Systems Inc., Madison, WI, USA, 2014; (c) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.

28 (a) Q. T. He, X. P. Li, L. F. Chen, L. Zhang and C. Y. Su, *ACS Catal.*, 2013, **3**, 1; (b) L. L. Zhang, Y. L. Nie, C. Hu and J. H. Qu, *Appl. Catal., B*, 2012, **125**, 418.

29 (a) N. Mizuno and K. Kamata, *Coord. Chem. Rev.*, 2011, **255**, 2358; (b) L. Y. Fan, Y. Y. Hong, J. Cao and C. W. Hu, *RSC Adv.*, 2016, **6**, 56656.