Correlation between redox properties and component of multicomponent heteropolysilicates with the same structure

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A series of the multicomponent heteropolysilicates with the same structure has been synthesised by a controllable method. Studies on the correlation between the redox properties and composition of the polyoxometalates indicate that the character of the addenda ion has the highest influence on the oxidising ability of the heteropolyanions for a given structure, and by comparison, the effects of the number of the addenda ions and the charge of the whole heteropolyanions were not completely prominent in mixed-addenda tungstomolybdosilicate heteropolyanions. For transition metal-substituted heteropolyanions, however, the effect of the number of the addenda ions is an important factor and stronger than that of the character of the addenda ion (transition metal ion) in some cases. On the other hand, incorporation of a transition metal ion can lead to a decrease of the reversibility of redox for heteropolyanions.

The designed preparation of materials at the level of molecules and atoms is a great challenge in the current science and technology. Considerable efforts to design and prepare new materials with well defined structures and desired properties are continuing world-wide.[1-5] However, up to now, the preparation of such novel materials is mainly guided by the intuition and experience of the synthetic chemist, which consumes a great of time and energy.[6]

The magnitude of this synthetic challenge reflects the lack of current knowledge about the true correlation between chemical manipulation in preparation, component and structure of a material, and the functionality that it displays, which provides a limited range for design. The key to improving this situation lies in producing materials with well defined composition, structure and physicochemical properties that have been incontrovertibly characterised under operating conditions. Unfortunately, at present, such materials prepared by well known methods have not been reported. Therefore, the preparation of incontrovertibly characterised materials and the investigation of the one-to-one relationship between their composition, structure, physicochemical properties and other functionalities are critical to advances in designing and synthesising new materials.

In 1987, Misono[7] proposed that the polyoxometalates (abbreviated to POMs) were suitable materials for both the design of catalysts for practical processes and for fundamental research regarding heterogeneous catalysis, owing to the relationships among the following four levels of information established on a molecular basis, namely, (i) catalytic performance; (ii) chemical and physical properties; (iii) molecular and bulk composition and structure; and (iv) method of synthesis of catalysts. These relationships are most useful for the molecular design of the solid materials and as a model system for fundamental research, providing opportunities for mechanistic studies at the molecular level. At the same time, polyoxometalates compounds have become increasingly important in applied catalysis. However, practical catalysts prepared by molecular design have hitherto not been realised. This may be because the understanding and study of the relationship between their composition, structure, chemical properties, physical function and the manipulation in synthesis were not quite sufficient.

In this paper, a series of multicomponent heteropolysilicates with the same structure has been synthesised by a controllable method. The correlation between the redox properties and composition of the polyoxometalates has been investigated by a cyclic voltammetric method in a systematic way. It is hoped to accumulate a substantial body of physicochemical data for polyoxometalates so that their true potential as materials for artificially designed manufacture can be released.

Experimental

Materials

$H_4[SiMo_{12}O_{40}]$. XH_2O and $H_4[SiW_{12}O_{40}]$. XH_2O were prepared and purified according to the literature methods.[8] Transition metal substituted tungstomolybdosilicates were prepared as follows. Tungstomolybdosilic acid crystals $H_4[SiMo_{12-m}W_mO_{40}]$. $X H_2O$ ($m = 2, 4, 6, 8, 10$), synthesised as a previous report,[9] were dissolved in water, and heated it up to 60–80°C by a water-bath. The transition metal nitrate (a little more than the stoichiometric value) was added to the tungstomolybdosilicic acid solution. The pH value of the mixture solution was adjusted to 3.8–4.5 as $m = 2, 4$; 4–4.7 as $m = 4$; 4.6–4.8 as $m = 6$; 4.7–5.0 as $m = 8$, and 4.8–5.1 as $m = 10$ with an aqueous solution of KAc-HAc (KAc:HAc:H_2O = 15 : 3 : 30). The reaction mixture was stirred for 30 min at constant temperature (60–80°C), then filtered. The filtrate was allowed to stand in a refrigerator at 0–3°C for 24 hours. The crystals were formed in approximately 80% yield based on the tungstomolybdosilicic acid.

All reagents used were of analytical reagent grade and without further purification.

Apparatus and procedures

Cyclic voltammetric experiments were carried out with a CHI 660A electrochemical workstation (CH instruments, China). A conventional three-electrode, one-compartment cell was used, with a 0.07 cm^2 glassy carbon(GC) disk electrode as working electrode, a twisted platinum wire as counter electrode and a Ag/AgCl (saturated KCl) as reference electrode. The GC working electrode was polished with 3 nm Al_2O_3 power and then washed with deionised water in an ultrasonic bath. Buffer solutions of pH 4.0 consisted of 0.2M solutions of CH_3COOK and CH_3COOH mixtures and buffer solutions of pH 3.3 were 0.2M H_2SO_4 + Na_2SO_4 mixtures. The solutions were deaerated thoroughly for at least 20 min with pure dinitrogen and kept under a positive pressure of this gas during the experiments. Potentials without specific marking were all measured and reported vs. Ag/AgCl electrode. The cyclic voltammetric patterns were obtained after multi-cycle scanning of the potential ranges indicated. All of the experiments were run at ambient temperature.

Component analysis was performed as follows. Transition elements were estimated by DTPA titration (back-titration with standard zinc solution, in pH 9.5 buffer in presence of Zn-agent). Molybdenum and tungsten in the same compound were separated by the method as described elsewhere,[10] then molybdenum was weighed as MoO_3 after precipitation with α-benzoinoxime and tungsten was weighed as WO_3 after precipitation with cinchonine. Potassium was weighed as $K[B(C_6H_5)_4]$ and silicon was estimated according to ref. 11; the water content was estimated by TG.

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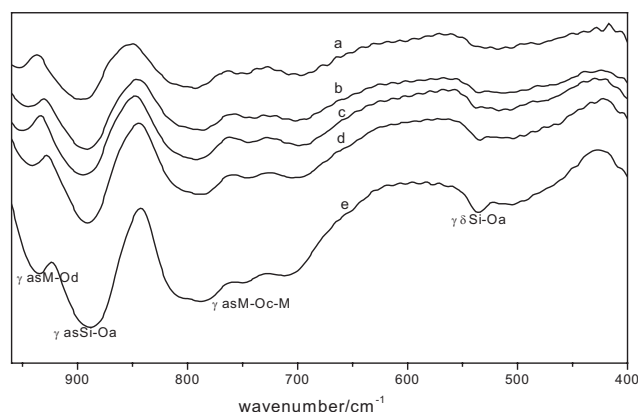
IR spectra of the samples, as pressed KBr pellets, were recorded on a NEXUS 670 FT-IR spectrophotometer (Nicolet, U.S.A.) in the 400–4000 cm⁻¹ region. Measurements of X-ray photoelectron spectra (XPS) were performed on a PHI-5100 X-ray photoelectron spectrometer, using an Al/ Mg bianode.

Results and discussion

Composition and structure analysis

$H_4[SiW_{12}O_{40}]$, $H_4[SiMo_{12}O_{40}]$, $H_4[SiMo_{10}W_2O_{40}]$, $H_4[SiMo_8W_4O_{40}]$, $H_4[SiMo_6W_6O_{40}]$, $H_4[SiMo_4W_8O_{40}]$ and $H_4[SiMo_2W_{10}O_{40}]$ were prepared by known methods. Their stoichiometric composition and the intact Keggin structure of the anion were further confirmed by IR spectra. In order to definitely characterise as-synthesised compounds $K_6[SiMo_{11-n}W_nM(H_2O)O_{39}]\cdot XH_2O$, their IR and XPS spectra and component analysis were investigated in detail. The related results were shown in Tables 1, 2 and Fig. 1 respectively. Their single crystal structures have already been determined by single-crystal X-ray diffraction.[12,13]

Table 1 lists the result of component analysis of the as-prepared POMs, and which indicates that the general formula of the polyoxometalates is: $K_6[SiMo_{11-n}W_nM(H_2O)O_{39}]\cdot XH_2O$ (n = 2, 4, 5, 7, 9; $M = Cu^{2+}$, Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}). The experimental data are consistent with the theoretical values.

The IR spectra of the transition metal-substituted tungstomolybdosilicates are shown in Fig. 1. The characteristic absorption bands of the Keggin structure are observed in the range 400–1100 cm⁻¹, *e.g.*, $v_{as}M-O_d$ (943–955 cm⁻¹); $v_{as}Si-O_a$ (893–900 cm⁻¹); $v_{as}M-O_c-M$ (700–800 cm⁻¹); $v_\delta Si-O_a$ (540–550 cm⁻¹). This result indicates that transition metal-substituted tungstomolybdosilicates possess a perfective Keggin structure and the framework of the tungstomolybdosilic acid anion is not damaged during its degradation and coordination with a transition metal ion in the procedure of preparation. In comparison with IR spectra of the corresponding tungstomolybdosilicic acids,[14] it is found that the $v_{as}M-O_b-M$ bands in all transition metal–substituted tungstomolybdosilicates disappeared, and $v_{as}M-O_c-M$ bands are split. These phenomena indicate that the M^{2+} instead of Mo^{6+}/W^{6+} make the anions more negative and of lower symmetry.

The results of XPS of a part of the compounds in Table 2 testified that the oxidation state of each component element in the transition metal-substituted tungstomolybdosilicates is + 4 to silicon, + 6 to tungsten and molybdenum, –2 to oxygen and + 2 to the transition metal element. Moreover, it can be seen from Table 2 that the binding energies of the electrons in the inner shell of the transition metal ions in POMs are higher than that of their oxides, e.g. in CoO, the binding energies of the electron in the inner shell of $2P_{3/2}$ and $2P_{1/2}$ of Co are 780.00 eV and 795.50 eV respectively, but they become 780.83 eV and 797.09 eV in $K_6[SiMo_9W_2Co(H_2O)O_{39}]$. The increase of binding energies demonstrates that the electron density around the transition element decreases and a part of the negative charge on the transition element moves to the polyoxometalate ligands.

Electrochemical investigation

It is well known that the pH of electrolytic media is a major influence on their electrochemical behaviour.[15] For the sake of comparison of equality, cyclic voltammetry measurements of the POMs investigated were performed in buffer

Fig. 1 IR spectra of (a) $K_6[SiMo_9W_2Cu(H_2O)O_{39}]$, (b) $K_6[SiMo_7W_4Cu(H_2O)O_{39}]$, (c) $K_6[SiMo_6W_5Cu(H_2O)O_{39}]$, (d) $K_6[SiMo_4W_7Cu(H_2O)O_{39}]$, and (e) $K_6[SiMo_2W_9Cu(H_2O)O_{39}]$.

Table 1 Results of component analysis for the POMs synthesised

POMs	M	Si	Mo	W	H₂O	K/%
$K_6[SiMo_9W_2Cu(H_2O)O_{39}]\cdot22H_2O$	(2.5)2.5	(1.1)1.1	(34.3)34.3	(14.6)14.6	(16.4)16.4	(6.2)6.2
$K_6[SiMo_9W_2Mn(H_2O)O_{39}]\cdot24H_2O$	(2.2)2.2	(1.1)1.1	(33.9)33.8	(14.4)14.4	(17.7)17.9	(6.1)6.15
$K_6[SiMo_9W_2Ni(H_2O)O_{39}]\cdot19H_2O$	(2.4)2.4	(1.1)1.2	(35.1)35.1	(14.95)14.9	(14.5)14.5	(6.3)6.25
$K_6[SiMo_9W_2Co(H_2O)O_{39}]\cdot26H_2O$	(2.3)2.2	(1.1)1.1	(33.4)33.4	(14.2)14.2	(18.8)18.8	(6.0)6.1
$K_6[SiMo_9W_2Zn(H_2O)O_{39}]\cdot25H_2O$	(2.5)2.5	(1.1)1.1	(33.5)33.5	(14.3)14.3	(18.2)18.0	(6.1)6.1
$K_6[SiMo_9W_2Cd(H_2O)O_{39}]\cdot24H_2O$	(4.3)4.3	(1.1)1.1	(33.2)33.1	(14.1)14.1	(17.3)17.3	(6.0)6.0
$K_6[SiMo_7W_4Cu(H_2O)O_{39}]\cdot21H_2O$	(2.4)2.3	(1.05)1.1	(25.1)25.1	(27.5)27.5	(14.8)14.8	(5.8)5.8
$K_6[SiMo_6W_5Cu(H_2O)O_{39}]\cdot23H_2O$	(2.3)2.3	(1.0)1.0	(20.55)20.6	(32.8)32.8	(15.4)15.4	(5.6)5.5
$K_6[SiMo_4W_7Cu(H_2O)O_{39}]\cdot22H_2O$	(2.15)2.1	(0.95)0.95	(13.0)13.0	(43.5)43.5	(14.0)14.0	(5.3)5.2
$K_6[SiMo_2W_9Cu(H_2O)O_{39}]\cdot21H_2O$	(2.0)2.0	(0.9)0.9	(6.2)6.2	(53.1)53.1	(12.7)12.8	(5.0)5.0
$K_6[SiMo_7W_4Co(H_2O)O_{39}]\cdot21H_2O$	(2.2)2.2	(1.05)1.0	(25.1)25.1	(27.5)27.6	(14.8)14.6	(5.85)5.8
$K_6[SiMo_6W_5Co(H_2O)O_{39}]\cdot22H_2O$	(2.1)2.1	(1.0)1.0	(20.7)20.7	(33.1)33.1	(14.9)14.9	(5.6)5.6
$K_6[SiMo_4W_7Co(H_2O)O_{39}]\cdot23H_2O$	(2.0)2.0	(0.95)0.95	(12.9)12.9	(43.3)43.3	(14.3)14.5	(5.3)5.3
$K_6[SiMo_2W_9Co(H_2O)O_{39}]\cdot23H_2O$	(1.9)1.9	(0.9)0.9	(6.1)6.1	(52.9)52.9	(13.2)13.25	(5.0)5.0

Theoretical values are given in parentheses.

Table 2 Binding energies of electron in the inner shell of constituent elements for POMs

POMs	Si	W	Mo	O	M	M
	$2p_{3/2}$	$4f_{7/2}$	$3d_{5/2}$	1s	$2p_{3/2}$	$2p_{1/2}$
$K_6[SiMo_9W_2Ni(H_2O)O_{39}]$	102.01	34.60	232.74	530.65	855.99	873.70
$K_6[SiMo_9W_2Zn(H_2O)O_{39}]$	101.42	35.51	232.69	530.42	1021.75	1044.78
$K_6[SiMo_9W_2Cd(H_2O)O_{39}]$	102.33	36.15	233.37	531.10	405.71	412.68
$K_6[SiMo_9W_2Co(H_2O)O_{39}]$	101.78	35.73	232.91	530.78	780.83	797.09
$K_6[SiMo_4W_7Cu(H_2O)O_{39}]$	102.33	36.15	233.69	531.28	935.15	954.86

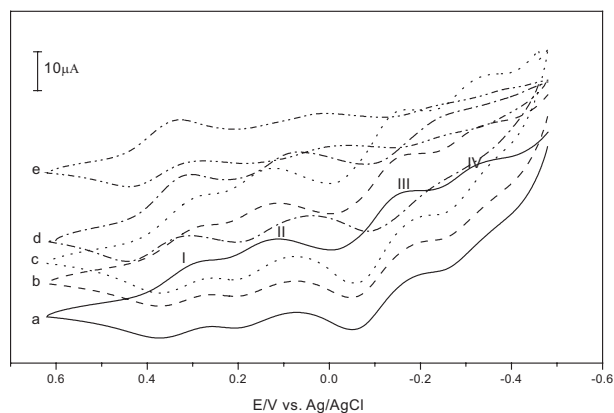**Fig. 2** Cyclic voltammogram at a glassy carbon electrode of 1 mM $H_4[SiW_{12}O_{40}]$ in 0.2M KAc-HAc buffer solution (pH = 4.00) in potential scan ranges from –0.05 to –1.00 V. Scan rate = 100 mV s^{-1}.

Fig. 3 Cyclic voltammogram at a glassy carbon electrode of 1 mM $H_4[SiMo_{12}O_{40}]$ in 0.2M H_2SO_4 + Na_2SO_4 solution in potential scan ranges from 0.33 to –0.37 V: solid line curve: pH = 3.3; dot curve: pH > 3.3. Scan rate = 100 mV s^{-1}.

solutions of pH 4.0, since the transition metal substituted tungstomolybdosilicates are stable in aqueous solutions at pH 3.5–5.1.
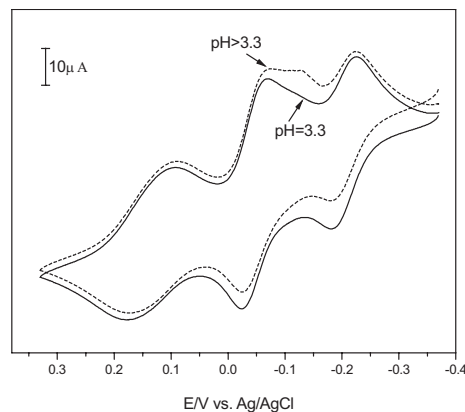
Cyclic voltammetric behaviour of $H_4[SiW_{12}O_{40}]$ & $H_4[SiMo_{12}O_{40}]$
Figure 2 presents the cyclic voltammograms of 1 mM $H_4[SiW_{12}O_{40}]$ in buffer medium of pH 4.0. The first two one-electron reduction waves, appearing at –0.24V and –0.50 V respectively, are pH-independent and slightly move to more negative potentials as compared with that in 1M perchloric acid.[16] However, a remarkable negative move is observed for the third wave located at a reduction potential of –0.92V vs Ag/AgCl in the buffer solution.

For $H_4[SiMo_{12}O_{40}]$ it is difficult to obtain well-defined redox waves by cyclic voltammetry in pH 4.0 aqueous solution owing to self degradation. It was reported that the first two-electron reduction wave of $H_4[SiMo_{12}O_{40}]$ was shifted to more negative potentials with increasing pH and eventually split into two one-electron waves at pH 2.4.[15] At pH > 3.3, a shoulder peak of the second cathodic wave is observed (see Fig. 3), which indicates the part decomposition of $H_4[SiMo_{12}O_{40}]$ and appearance of other species. Hence, we obtained the reduction peak potential of the first one-electron wave located at 0.09 V vs Ag/AgCl in 0.2 M Na_2SO_4–H_2SO_4 solution of pH 3.3.

Fig. 4 Cyclic voltammogram at a glassy carbon electrode of (a) $H_4[SiMo_{10}W_2O_{40}]$, (b) $H_4[SiMo_8W_4O_{40}]$, (c) $H_4[SiMo_6W_6O_{40}]$, (d) $H_4[SiMo_4W_8O_{40}]$, and (e) $H_4[SiMo_2W_{10}O_{40}]$ in 0.2M KAc-HAc buffer solution (pH = 4.00) in potential scan ranges from 0.62 to –0.48 V. Scan rate = 100 mV s^{-1}.

*Cyclic voltammetric behaviour of $H_4[SiMo_{12-m}W_mO_{40}]$*
The cyclic voltammograms of the tungstomolybdosilic heteropoly acids $H_4[SiMo_{12-m}W_mO_{40}]$ (m = 2, 4, 6, 8, 10) in pH 4.00 buffer solutions are shown in Fig. 4. All of which begin with two-step one-electron waves, and the first reduction wave potential is observed at 0.300, 0.302, 0.306, 0.317, and 0.338 V vs. Ag/AgCl for m = 2, 4, 6, 8, 10, respectively. The first two one-electron reduction peak potentials of these heteropolyanions move toward much more positive potential by comparison with those of $H_4[SiW_{12}O_{40}]$ and $H_4[SiMo_{12}O_{40}]$. The separation of the anodic and cathodic peak potentials of the first two redox couples for $H_4[SiMo_{10}W_2O_{40}]$, $H_4[SiMo_8W_4O_{40}]$ and $H_4[SiMo_6W_6O_{40}]$ was about 60±5 mV, which indicates the reversible nature of the one-electron wave. However, the peak potential separation for the first two redox couples of $H_4[SiMo_4W_8O_{40}]$ and $H_4[SiMo_2W_{10}O_{40}]$ was more than 100 mV, which implies that each one-electron wave may be quasi-reversible.

Cyclic voltammetric behaviour of transition metal substituted tungstomolybdosilicates
When a transition metal ion, such as Cu^{2+} or Co^{2+} with a small radius, replaces addenda ions Mo^{6+}/W^{6+} incorporated in the tungstomolybdosilicates, it resides in an octahedral environment with one coordination site occupied by a labile water molecule, which differs from that of the others, whereas the coordinated environments of addenda ions (Mo^{6+}/W^{6+}) in non-substituted tungstomolybdosilicates are all same. As a result, non-substituted tungstomolybdosilicates can be considered as really "saturated" substituted heteropolyanions or "mixed addenda" heteropolyanions, while tungstomolybdosilicates substituted by transition metal ions, such as Co^{2+} or Cu^{2+}, are not. This difference is important and its effects on the electrochemical behaviours of the polyoxometalates are very remarkable. The detailed electrochemical characters of the respective heteropolyanions will be described as follows.

Figure 5 shows the cyclic voltammogram of 1 mM Co-substituted tungstomolybdosilicates in pH 4.00 buffer solutions at a scan rate of 100 mV s^{-1}. Two one-electron redox couples appear in the positive potential direction, and the first reduction peak potentials of $K_6[SiMo_9W_2Co(H_2O)O_{39}]$, $K_6[SiMo_7W_4Co(H_2O)O_{39}]$, $K_6[SiMo_6W_5Co(H_2O)O_{39}]$, $K_6[SiMo_4W_7Co(H_2O)O_{39}]$ and $K_6[SiMo_2W_9Co(H_2O)O_{39}]$ appear at 0.256 V, 0.279V, 0.282V, 0.302V and 0.312V respectively, more negative potentials as compared with the tungstomolybdosilic heteropoly acids, owing to the increase in the negative charges of the heteropolyanions after substituting a Co^{2+} for a Mo^{6+} or W^{6+} in them.
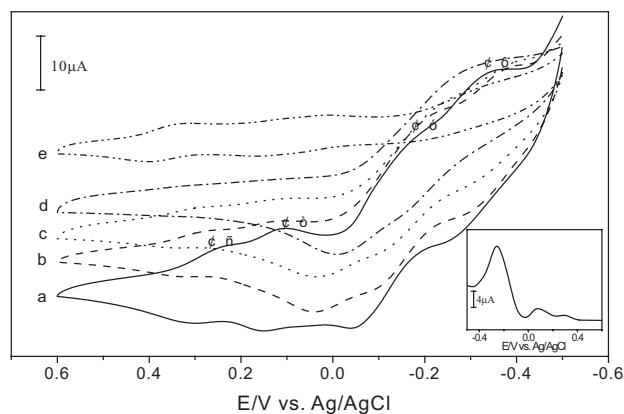
Fig. 5 Cyclic voltammogram at a glassy carbon electrode of (a) $K_6[SiMo_9W_2Co(H_2O)O_{39}]$, (b) $K_6[SiMo_7W_4Co(H_2O)O_{39}]$, (c) $K_6[SiMo_6W_5Co(H_2O)O_{39}]$, (d) $K_6[SiMo_4W_7Co(H_2O)O_{39}]$, and (e) $K_6[SiMo_2W_9Co(H_2O)O_{39}]$ in 0.2M KAc-HAc buffer solution (pH = 4.00) in potential scan ranges from 0.60 to -0.50 V. Scan rate = 100 mV s^{-1}. The insert is the reduction process of 1 mM $K_6[SiMo_4W_7Co(H_2O)O_{39}]$ in 0.2M KAc-HAc buffer solution at pH 4.0 using differential pulse voltammetry, which indicates the reduction began at 0.302V vs Ag/AgCl.

By comparison with the corresponding heteropoly acids, it is noteworthy that the transition metal ions introduced into the heteropolyanions evidently increase their irreversibility of redox behaviour (see Fig. 5). In contrast with those of $H_4[SiMo_{10}W_2O_{40}]$, the reversibility of the four redox couples for $K_6[SiMo_9W_2Co(H_2O)O_{39}]$ exhibits a decreasing tendency. When the number of the contained tungsten atoms was further increased, the decreasing tendency of the reversibility was more and more obvious. Cyclic voltammetric behaviour of other transition metal substituted tungstomolybdosilicates is similar to that of Co-substituted tungstomolybdosilicates; the first reduction peak potentials are summarised in Table 3.

Correlation between redox properties and component
The well known Keggin structures $(XM_{12}O_{40}^{n-}$ where X = central ion or heteroatom; M = addenda atom or ion), including mixed addenda Keggin structure heteropolyanions, and the structure of transition metal-substituted Keggin structure heteropolyanions are illustrated in Fig. 6. The redox behaviours of heteropolyanions with the Keggin structure have been extensively investigated, and the following conclusions have resulted from numerous investigations.
1. If the constituent elements of the polyanions are the same, their oxidising ability increases in the sequence α, β-, γ-isomers according to the number of rotated M_3O_{13} groups.[15,17-19]
2. When the structures and addenda atoms of the polyanions
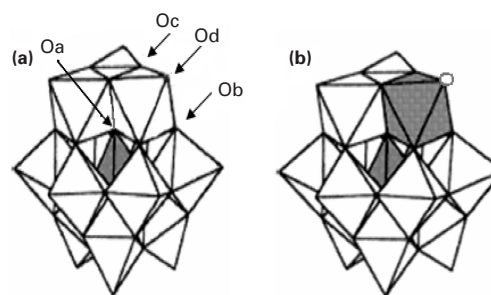
Fig. 6 (a) Structure of Keggin anion α- $[XM_{12}O_{40}]^{n-}$: terminal (O_d), edge-bridging (O_c), corner-bridging (O_b), tetrahedral (O_a) oxygen atoms, and (b) transition metal-substituted Keggin structure anion α- $[XM_{11}O_{39}M'L)]^{m-}$. Each white octahedron represents a MO_6 group, and each dark tetrahedron represents a XO_4 group. The dark octahedron in b contains an incorporated transition metal ion M' and the open circle represents L coordinated to M'

are identical, their oxidising ability decreases with a decrease in the valence of the central ions.[15,17,19-21]
3. Among the mixed-addenda heteropolyanions or the heteropolyanions containing different addenda ions with same central ion and structure, the oxidising ability depends mostly on the addenda ion and can be ordered by the oxidising ability of the addenda ions.[15,22]
4. For the transition metal-substituted heteropolyanions, such as $XM_{12-n}M'_nLO_{39}^{m-}$ [X = Si or P; M = Mo(VI) or W(VI); M' = incorporated transition metal ion or substitute, such as Al(VI); Ni(VI); Fe(VI); Cu(VI); Co(VI); L = water or other organic molecules], the oxidising ability decreases with decreasing oxidation number for the substituent (M').[15,23,24]

These interesting studies on the redox chemistry of the heteropolyanions may help in understanding the reactivity and mechanistic behaviour of the heteropolyanions as redox reagents and realising artificial design of catalysts by using polyoxometalates as a model. Nevertheless, research on the effect of the amount of the substituent present in a mixed-addenda species, or transition metal-substituted heteropolyanions, on the oxidising ability of the heteropolyanions is very scarce. Herein, investigation into the relationship between the component of the multicomponent heteropolysilicates with the Keggin structure and their oxidising ability will have the potential to fill this gap.

The first reduction peak potential data, which can be deemed to be the oxidising ability criterion, for the multicomponent heteropolysilicates, are summarised in Table 3. By comparison with $H_4[SiW_{12}O_{40}]$ and $H_4[SiMo_{12}O_{40}]$, using the data in Table 3 and the results reported by Fruchart,[23] three notable features can be found.

Table 3 First reduction peak potentials (E/V vs Ag/AgCl) for multicomponent heteropolyanions in pH 4.0 buffer solution[a]

	Cu^{2+}	Co^{2+}	Ni^{2+}	Cd^{2+}	Zn^{2+}	Mn^{2+}	–
9/2	0.277	0.256	0.255	0.238	0.237	0.225	–
7/4	0.283	0.279	–	–	–	–	–
6/5	0.285	0.282	–	–	–	–	–
4/7	0.315[b]	0.302[b]	–	–	–	–	–
2/9	0.320	0.312	–	–	–	–	–
12/0	–	–	–	–	–	–	0.092
10/2	–	–	–	–	–	–	0.300
8/4	–	–	–	–	–	–	0.302
6/6	–	–	–	–	–	–	0.306
4/8	–	–	–	–	–	–	0.317
2/10	–	–	–	–	–	–	0.338
0/12	–	–	–	–	–	–	−0.240

[a]M' represents the transition metal ion substituted; Mo/W represents (the number of Mo atom)/(the number of W atom) in the heteropolyanions.
[b]The data are read from differential pulse voltammetry.

1. The first reduction wave potentials of the tungstomolybdosilicate heteropolyanions move toward more positive potentials, exhibiting first a sharply increasing and then a slowly decreasing tendency with increase of the number of the molybdenum atoms contained in the anion (Fig. 7). The largest potential shift is 0.578V more positive than that of $H_4[SiW_{12}O_{40}]$ and 0.248V more positive than that of $H_4[SiMo_{12}O_{40}]$. This phenomenon may be ascribed to the more reducible character of molybdenum and the synergistic effect of the molybdenum and the tungsten in the tungstomolybdosilicate anions. This synergistic effect could originate from the increase of the stability of highly reduced states upon asymmetric substitution from W–O–W or Mo–O–Mo to Mo–O–W.[25,26] When the number of the contained molybdenum atoms was further increased, the more characteristics of the bonding and structure of $H_4[SiMo_{12}O_{40}]$ materialised in the tungstomolybdosilicate anion. This could explain why the first reduction wave potential of the tungstomolybdosilicate anion falls slowly off after the peak value reached with increasing the number of the molybdenum atoms. However, the mechanism of the synergistic effect is still not clarified.[25,26]

2. Incorporation of the transition metal ion (M^{2+}) depressed the oxidising ability of the tungstomolybdosilicate anion, owing to increasing the negative charge of the whole heteropolyanion. For a given oxidation state of transition metals, the oxidising ability of the transition metal-substituted tungstomolybdosilicate anion increases with increasing electronegativity of the transition metal element (Fig. 8). However, the law of the corresponding variability controlled by the molybdenum atoms was not changed because the oxidising ability of these M^{2+} substituents is weaker than that of Mo^{6+}. These results indicate that the effect of increasing negative charge by incorporating the lower valence metal ion (M^{2+}) instead of the higher valence molybdenum or tungsten ion (Mo^{6+} or W^{6+}) is stronger than the synergistic effect between the addenda ions, and on the other hand, it could be counterbalanced or redeemed by the oxidising ability of the transition metal ions (see Table 3 and Fig. 8).

3. As the number of the tungsten atoms contained in the anion increases, the reversibility of redox for tungstomolybdosilicate heteropoly acids decreases. The transition metal ions incorporated in heteropolyanions can give rise to increasing irreversibility of the redox.

Conclusion

In general, the oxidising ability of the heteropolyanions depends on many factors, such as the structure, component, counter cation, additives, solvent and pH of the media in the reactive system. At the same time, the interaction between
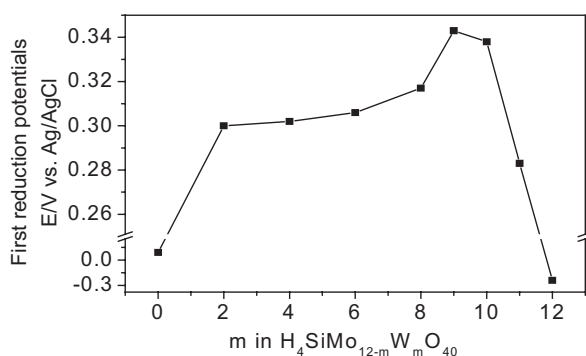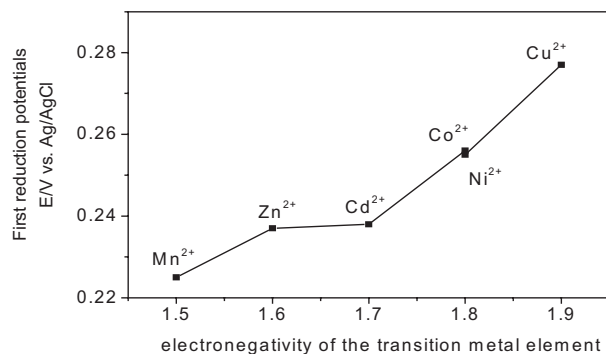
Fig. 8 Plot of the first reduction potential of $K_6[SiMo_9W_2M'(H_2O)O_{39}]$ vs. electronegativity of the incorporated transition metal element. The data of electronegativity of transition metal ions are taken from ref. 30.

the various factors is ubiquitous. Such complexity not only provides scope for modulation of the oxidising ability of the heteropolyanions, but also offers a challenge to the researcher pursuing design preparation. A number of the studies on the redox chemical behaviour of the heteropolyanions have been reported.[27-29] However, there is an obvious lack of the available data that could be used in design. Our results indicate that the character of the addenda ion has the highest influence on the oxidising ability of the heteropolyanions for a given structure, and by comparison, the effect of the number of the addenda ions and the charge of the whole heteropolyanions were not completely prominent in the mixed-addenda tungstomolybdosilic heteropolyanions. However, for the transition metal-substituted heteropolyanions, the effects of the number of the addenda ions is indeed a remarkable factor and stronger than those of the character of the addenda ion (transition metal ion) in some case (see Table 3). On the other hand, incorporation of the transition metal ion can lead to decrease of the reversibility of redox for heteropolyanions. These conclusions may be useful in the selection and design of redox catalysts for a desired reaction.

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Fig. 7 The first reduction wave potential of the tungstomolybdosilicate heteropoly acids. The data of *m* = 9, 11 are taken from ref. 23.

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