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Involvement of heteroatoms in charge transfer of Keggin-type heteropolyanion

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Spectroscopic measurements of an electrochemically deposited film from a Keggin-type heteropolyanion solution indicate that electron transfer takes place not only on polyatoms but also on heteroatoms of silicon.

Keggin-type heteropolyanions are known to permit multiple electron transfer without the accompanying change in skeleton structure,[1] and attention is focused on the application of heteropolyanions to a catalyst for electrochemical reaction. A well-defined cyclic voltammogram of heteropolyanion has been obtained in a mixed organic and aqueous solution, in which dioxane and tetrahydrofuran are exclusively used as the organic solvent since the reduced polyanion is stabilized by forming an adduct with their cyclic ethers.[2,3] For example, $[SiMo_{12}O_{40}]^{4-}$ (denoted as $SiMo_{12}$) undergoes five reversible two-electron reactions on cathodic scan up to −0.3 V *vs.* SCE in a 1,4-dioxane (50 vol%) + water (50 vol%) solution containing 0.5 M H_2SO_4.[3] For these electrode reactions, it is generally considered that the electron transfer is charged wholly with polyatoms. That is, heteroatoms are not reducible electrochemically except for particular transition metals (Co^{3+}, Fe^{3+}, *etc.*) in 12-polytungstates.[4,5] However, we present here spectroscopic evidence that typical heteroatoms as well as polyatoms are involved in the electron transfer of heteropolyanion. In this study, $SiMo_{12}$ was electroreduced to a thin oxide film with an Au electrode, and X-ray photoelectron spectrum of Si 2p showed the existence of Si species with lower valence states in the deposited film, indicating that the quadrivalent silicon atoms were reduced during the electrochemical reduction.

Sodium 12-molybdosilicate ($Na_4SiMo_{12}O_{40}$) was purchased from Nippon Inorganic Colour & Chemical Co. All solutions were prepared with doubly distilled water and deaerated by bubbling purified nitrogen gas before use. Electrochemical experiments were performed in a beaker-type cell equipped with an Au working electrode, a platinum auxiliary electrode, and an Ag/AgCl/saturated KCl electrode. A thin oxide film was deposited on an Au foil (10 mm × 10 mm) or rod (1 mmϕ × 3 cm) electrode by cycling the potential between 0 and −0.7 V for 3 h at a scan rate of 10 mV s^{-1} in an aqueous solution of pH 3 with 0.2 mM $Na_4SiMo_{12}O_{40}$ and 0.5 M Na_2SO_4. The film-coated electrode was rinsed with deaerated water, and immediately dried under vacuum. The sample electrode thus obtained was exposed to air for a given period of time. The film thus prepared was characterized by Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS). XPS spectra were collected using a Fisons Escalab 210 spectrometer, with an $Al(K_\alpha)$ unmonochromatic source (15 kV, 20 mA). The binding energy scale was calibrated with respect to the C 1s (284.8 eV) signal. A mixture of Gaussian and Lorentzian functions was used to fit Si 2p, Mo 3d and O 1s spectra. Electron spin resonance (ESR) spectra were measured on the film deposited onto a rod electrode with a JEOL JES-FE1X spectrometer operating at X-band frequency (9.47 GHz) at room temperature.

Fig. 1a shows an IR spectrum of pure $SiMo_{12}$ obtained in the transmission mode. This spectrum consists of four peaks at 962 (ν(Mo=$O_{terminal}$)), 912 (ν(Si–O)), 869 (ν(Mo–O–Mo, bridge between corner-sharing octahedra)) and 782 cm^{-1} (ν(Mo–O–Mo, bridge between edge-sharing octahedra)), which are typical of a Keggin-type complex.[6,7] Curve b is the reflection spectrum of the as-deposited film, and curves c, d and e are the spectra obtained after the film-deposited electrode was previously exposed to air for the indicated time. In curve b, the bands observed at 982 and 765 cm^{-1} are due to Mo=O and Mo–O–Mo vibrational modes, respectively, and the bands at 1137 and 1052 cm^{-1} to the metal–OH vibration.[8] There is no absorption band for the Si–O bond. Hence, it is suggested that the as-deposited film consists of the oxyhydroxide containing pentavalent molybdenum ($MoO_{3-x}(OH)_x$) and the structure is not Keggin-type but polymeric. After the exposure to air for 1 h (curve c), however, the band (912 cm^{-1}) corresponding to the Si–O vibration appeared and the optical intensity was enhanced with increasing the exposure time. Naturally, some amount of Si should be included in the deposited film, and the absence of the Si–O band for the as-deposited film may indicate that the Si–O bond of $SiMo_{12}$ was cleaved during the deposition to the film. The finding that the Si–O bond appeared after the deposited film was exposed to air may mean that Si atom combined again with Mo through oxygen atom. In fact, the peaks related to the Mo–O bonds were shifted during the growth of the Si–O band.

XPS spectra of the deposited film in the energy regions of Si 2p (A), Mo 3d (B) and O 1s (C) are shown in Fig. 2, where the exposure to air times were 0 (a) and 48 h (b). Pure $SiMo_{12}$ contains only Si^{4+} ions, and a singlet peak centered at the binding energy (BE) of 103.1 eV was observed (not shown). In Fig. 2A(a), we can see a feature obviously different from that of pure $SiMo_{12}$. The curve fitting of the spectrum gives three contributions at the lower BE side which are assignable to Si^{2+} (101.3 eV) as the main component, Si^{3+} (102.2 eV) and Si^0 (99.3 eV), along with the weak peak due to Si^{4+} (103.3 eV).[9] The existence of such Si species of lower valence states strongly suggests that electrons were trapped by silicon atoms to render the quadrivalence state to lower valence. As shown in Fig. 2A(b), however, the contribution due to Si^{4+} becomes notable upon the exposure to air, indicating the oxidation of lower valent silicon. These results are consistent with the view

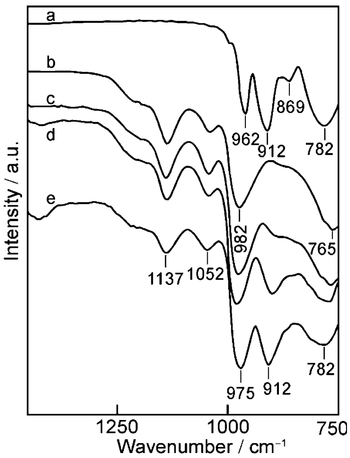

Fig. 1 FTIR spectra of pure $SiMo_{12}$ in KBr (a) and electrodeposited films (b to e). Spectra b to e were taken 0 (b), 1 (c), 6 (d) and 12 (e) after the film-coated electrode was exposed to air. The film was deposited on an Au electrode by cycling the potential at a scan rate of 10 mV s^{-1} between 0 and −0.7 V for 3 h in a 0.5 M Na_2SO_4 solution of pH 3.0 containing 0.2 mM $SiMo_{12}$.

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from the IR result that the Si–O bond is first cleaved in the electroreduction of $SiMo_{12}$ and then regenerated upon the exposure to air.

A doublet peak of spectrum a in Fig. 2B consists of four components arising from two valence states of Mo. The peaks observed at 231.4 and 234.7 eV are attributable to Mo^{5+}, while those at 232.6 and 236.0 eV to Mo^{6+}.[10] Upon the exposure to air (Fig. 2B(b)), the intensities of peaks corresponding to Mo^{5+} and Mo^{6+} decreased and increased, respectively. Therefore, it is indicated that a part of pentavalent molybdenum is oxidizable to hexavalent by air. On the other hand, the O 1s spectra (Fig. 2C) are composed of three components originating from oxide (O^{2-}), hydroxide (OH^-) and adsorbed water.[11] The large contribution due to hydroxyl oxygen in the as-deposited film is characteristic of oxyhydroxide species,[11,12] confirming the formation of Mo oxyhydroxide. A decrease in the O^{2-} content after the exposure to air can be associated with dissociative chemisorption of water which leads to a high surface concentration of hydroxide, rather than the film oxidation.[12]

To obtain more detailed information about Mo^{5+} ions in the deposited film, ESR spectra were measured for the samples prepared in various conditions (Fig. 3). No ESR signal was observed for pure $SiMo_{12}$ since this compound is composed of Mo^{6+} (d^0 configuration) ions. As shown in curve a, the as-deposited film exhibits a relatively isotropic signal with $g \sim 1.93$ (denoted A), attributable to pentavalent Mo (d^1). The intensity of this signal decreased with increasing the exposure time to air and completely disappeared after 48 h. According to the Mo 3d XPS data shown above, the disappearance of signal A can be ascribed to the partial oxidation of Mo^{5+} ions to ESR-silent Mo^{6+}. In curve d, a new signal (denoted B) with axial symmetry ($g_\perp = 1.930$, $g_\parallel = 1.881$) is observed, and the intensity of this signal was independent of the existence of signal A and the exposure time. Hence, it is considered that there are two kinds of pentavalent molybdenum in the deposited film: one is the Mo^{5+} ion which is oxidizable to Mo^{6+} by air and the other is stable and not subjected to air-oxidation. Because the g parameters of signal B are close to those of the Mo^{5+} ions in the polymeric Mo oxide phase,[13] the latter species can be ascribed to the Mo^{5+} ions in the Mo oxyhydroxide. We have previously reported that the similar electrolysis of $[PMo_{12}O_{40}]^{3-}$ led to the formation of Mo oxyhydroxide without P atoms.[14] This film gave an ESR signal basically the same as signal B, which was independent of air-treatment. This implies that the unstable Mo^{5+} ions giving signal A are in the vicinity of the reduced Si species.

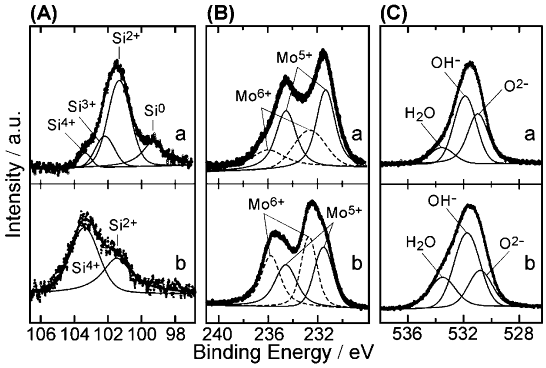

Fig. 2 XPS spectra of an electrodeposited film in the energy regions of Si 2p (A), Mo 3d (B) and O 1s (C), which were taken before (a) and after (b) the exposure to air for 48 h. The film was prepared by the same way as that in Fig. 1.

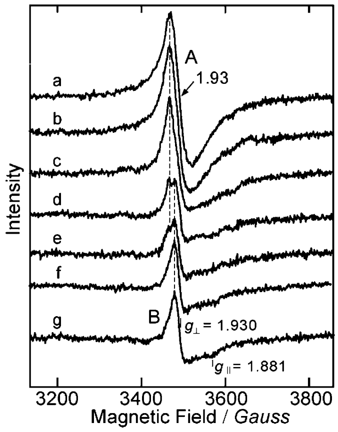

Fig. 3 ESR spectra of an electrodeposited film taken 0 (a), 1 (b), 6 (c), 12 (d), 24 (e), 48 (f) and 72 h (g) after the film-coated electrode was exposed to air. The film was prepared by the same way as that in Fig. 1.

The formation of two types of Mo^{5+} ions as noted above may be caused by different processes of charge compensation in the electroreduction of $SiMo_{12}$: (i) the incorporation of protons; (ii) the elimination of bridging oxygens. The charge compensation in the former case can be done by the hydrogenation of $Mo^{VI}{=}O$ to form Mo^{V}–OH, and the condensation of this species results in the formation of Mo–O–Mo linkage. In fact, it was reported that Mo oxyhydroxide can form by the electroreduction of MoO_4^{2-}.[15] Another type of charge compensation can be achieved by eliminating oxygen ions from metal oxide to generate an oxygen-deficient structure.[16,17] In the present study, the electrochemical reduction of $SiMo_{12}$ can be also charge-balanced by the elimination of O^{2-} from the Mo–O–Si linkage with the generation of lower valent silicon and unstable (oxidizable) pentavalent molybdenum.

In summary, the Si 2p XPS spectrum of the film electrochemically deposited from the Keggin-type heteropolyanion solution indicated that the electron transfer takes place not only on the Mo framework but also on the central Si atom. Evidence in support of this view was also presented from FTIR and ESR studies.

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