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A QUANTITATIVE ESR STUDY OF Mo^{5+} FORMED ON DODECAMOLYBDOPHOSPHORIC ACID

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The esr signal of Mo^{5+} on reduced 12-molybdophosphoric acid was found to be significantly affected by the degree of hydration, the degree of reduction (DR) and recording temperature. The spin concentrations of samples with low DR (< 1 e/anion) could quantitatively be measured when the relaxation time of Mo^{5+} was made sufficiently large by sample evacuation at 300°C followed by recording at -100°C. For samples with DR $>$ 1 e/anion the dilution of reduced anions with unreduced ones was effective. It was suggested that the interaction between Mo^{5+} ions within a polyanion remains weak even when 4 Mo^{5+} are produced in a polyanion.

It is expected that the esr spectra of Mo^{5+} on reduced 12-molybdophosphates provide important information on the coordination states and the redox mechanism of molybdenum. Despite some preliminary studies so far reported[1-3], the esr study of this system has remained almost unexplored from the view point of catalysis. Dodecamolybdophosphoric acid is capable of possessing a large number of H_2O molecules as the water of crystallization, which affects significantly the shape and intensity of the esr signals of Mo^{5+}. Leaving this point out of account, one can neither obtain proper esr signals nor measure quantitative spin concentrations. In the present study, we have tried to establish appropriate conditions for sample pretreatments and esr measurements as well as to get information on reduced 12-molybdophosphoric acid.

Dodecamolybdophosphoric acid was prepared by the method described previously[4]. The reduction of solid samples with H_2 was carried out in a conventional circulation system at 150°C after evacuation at the same temperature. The water formed during the reduction was removed off with a liq. N_2 trap. The degree of reduction was determined from the change of H_2 pressure. Electrolytic reduction of an aqueous solution of 12-molybdophosphoric acid (0.34 mol/l) was carried out in an H-type cell using cation exchange membrane as a diaphragm. The potential of a carbon cathode was controlled vs. an Ag/AgCl reference electrode by a potentiostat (Hokuto Denko, HA-303). The degree of reduction was determined from the electricity of the electrolysis. All the reduction procedure was carried out in an atmosphere of N_2. After the reduction, the solution was evacuated at room temperature for evaporation to dryness. Esr signals were recorded at -170 ~ 200°C on a JEOL JES-FE1X spectrometer equipped with a variable temperature controller (UCT 2AX). Samples were placed in a quartz tube (5 mm o.d.) connected to a glass stopcock and were evacuated at various temperature prior to measurements. Spin concentrations were determined by the double integration of esr signals using $VOSO_4$ (in $(NH_4)_2SO_4$) and DPPH (in benzene) as standards.

Some examples of esr spectra of partially reduced 12-molybdophosphoric acid are shown in Fig. 1. The shape and intensity of the Mo^{5+} signal were found to be strongly affected by the evacuation conditions of the reduced samples. A sharp signal with hfs was observed after evacuation at room temperature (a), which is attributed to Mo^{5+} of $I = 0$ (75%) and $I = \frac{5}{2}$ (25%). With a rise in evacuation temperature up to 200°C, not only the intensity increased but also the anisotropy of g-factor became obvious. This signal (denoted A) showed g-values ($g_{\perp} = 1.956$, $g_{\parallel} = 1.87$, $A_{\perp} = 43.6G$, $A_{\parallel} = 87.1G$), which disagreed with ones so far reported ($g_{\perp} = 1.953$, $g_{\parallel} = 1.947$)[1]. Another signal with $g_{\perp} = 1.940$ and $g_{\parallel} = 1.90$ (B) appeared after evacuation at 300°C (c), and became dominant after subsequent exposure to water vapour at room temperature (d). But further evacuation at 100°C again restored signal A (e). It is suspected that the signals (A) and (B) are ascribable to two Mo^{5+} states which are different in coordination number. Detailed analysis concerning this is now under investigation. We like to focus on the spin concentration in this communication.

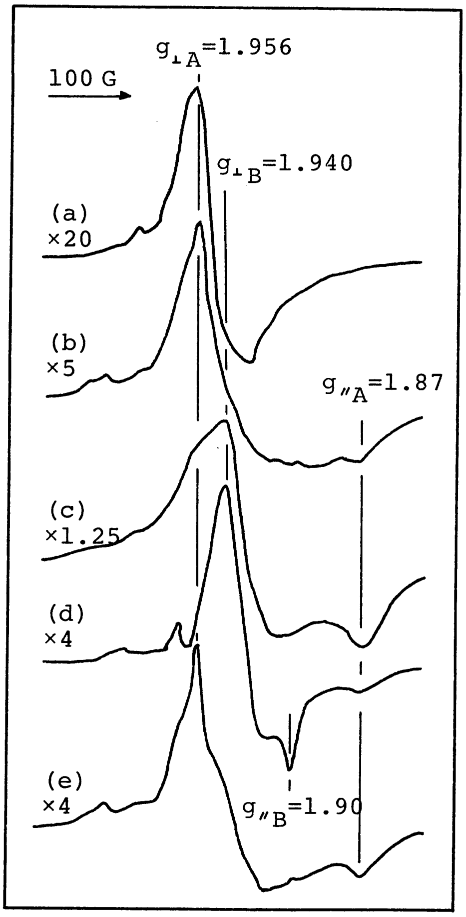

Fig. 1 Changes in the esr signal of reduced 12-molybdophosphoric acid (recorded at -100°C). Evacuated at (a) room temp. (b) 200°C (c) 300°C. (d) Exposed (c) to H_2O at room temp. (e) Evacuated (d) at 100°C. H_2 reduction : 150°C Degree of reduction : 0.6 e/anion

Apart from evacuation temperature, spin concentration was found to depend on recording temperature and the degree of reduction. Figure 2 shows the dependence of spin concentration on recording temperature, where the spin concentrations of reduced samples evacuated at 200 or 300°C are expressed as relative values normalized to those observed at -100°C. For both samples the spin concentrations were maximum and constant at recording temperatures -100 ~ 0°C, while they decreased gradually with further increase in recording temperature. The dependence on recording temperature can be accounted for by the spin-lattice relaxation effect. The above result indicates that the effect becomes negligible at temperatures below 0°C.

The effect of sample evacuation is clearly indicated in Fig. 3, where the spin concentration is plotted as a function of the degree of reduction: x that is defined as the number of introduced electrons per Keggin unit. It was found in a separate experiment that the evacuation at elevated temperatures not only gave rise to sample dehydration but also caused partial reduction. The extents of the evacuation-induced reduction were 0.01, 0.07 and 0.17 e/anion when unreduced samples were evacuated at 100, 200 and 300°C, respectively. The spin concentrations in Fig. 3 are corrected for such evacuation-induced reduction by deducting the above values from the observed ones. As shown in Fig. 3 only small fractions of Mo^{5+} were detected after evacuation

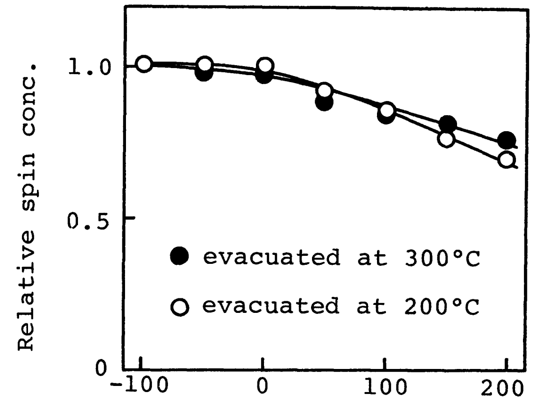

Fig. 2 Dependence of spin concentration on recording temperature.
Sample: 12-molybdophosphoric acid reduced with H_2 at 150°C
Degree of reduction: 0.6 e /anion

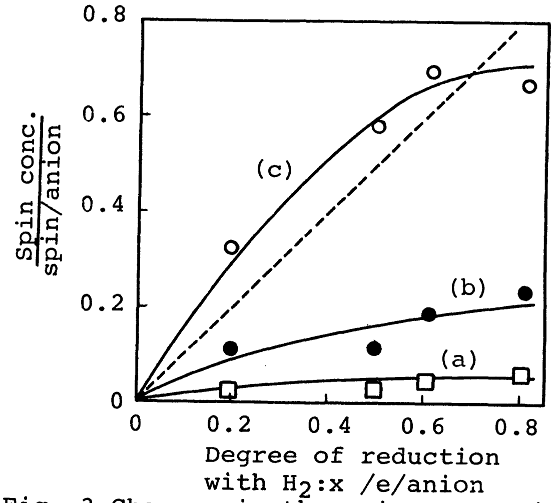

Fig. 3 Changes in the spin conc. with reduction degree of 12-molybdophosphoric acid evacuated at (a) 100°C (b) 200°C (c) 300°C
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at 100°C. The spin concentration increased with rasing evacuation temperature and reached nearly expected values at 300°C. Hall et al.[5] suggested that in the case of Mo^{5+} formed on MoO_3/Al_2O_3 only distorted Mo^{5+} species are observed by esr. This concept may well explain our results. Evacuation of samples, which results in dehydration of polyanions, appears to be effective for the transformation of highly symmetric species into distorted ones. Thermogravimetric analyses of reduced samples under evacuation conditions showed that while the water of crystallization was lost almost completely below 150°C, another step of dehydration occured between 200°C and 420°C, and that the weight decreases in the latter step were in agreement with the following type of dehydration[6].

$$H_3PMo_{12}O_{40-x}(OH)_x \ (I) \xrightarrow{200-420^\circ C} PMo_{12}O_{38.5-\frac{x}{2}} \ (II) + \frac{3+x}{2}H_2O \qquad (1)$$

That is, acidic protons as well as the protons introduced during the reduction are desorbed as H_2O molecules at the latter step, leaving oxygen vacancies in the polyanion. Considering that the spin concentration increases sharply by evacuation at the similar temperature region, it is likely that the Mo^{5+} species observed in Fig. 3 are attributed to the dehydrated one (II), not to the hydrated from (I). The importance of dehydrated form in esr measurements has also been pointed out by Mizuno et al.[7].

For samples with lower degrees of reduction ($x < 1$), one can obtain almost stoichiometric spin concentrations after evacuation at an adequate temperature as stated above. However, this is not the case for samples with higher degrees of reduction. Figure 4 shows the results of quantitative analysis for samples which were reduced electrochemically to various extents. Again the spin concentration increased with increasing evacuation temperature, but even after evacuation at 400°C, it remained far below the expected value for $x > 1$. The signals for $x > 1$ were significantly broadened to thousands gauss in magnetic field, and this is an apparent cause for the underestimation of spin concentration. The signal broadening suggests that spin-spin relaxation effects become significant. There are two possibilities in spin-spin relaxation depending on whether the interacting spins are in the same polyanion (intra-polyanion interaction) or in different polyanions (inter-polyanion interaction). According to our ir study[6], the electrochemical reduction of Keggin unit under the present conditions proceeds by a 4-electron step as follows. In this equation, valence states of Mo ions were determined by an XPS[8].

$$\underset{(\mathrm{III})}{H_3[PMo^{VI}_{12}O_{40}]^{3-}} \xrightarrow{+4H} \underset{(\mathrm{IV})}{H_3[PMo^{VI}_{8}Mo^{V}_{4}O_{36}(OH)_4]^{3-}} \qquad (2)$$

This means that, even at $x < 4$, the reduced sample is a mixture of reduced anions (4 e/anion) and unreduced ones and the rate of reaction between (III) and (IV) is negligibly small. The fact that the spin concentrations of samples with $x \leq 1$ coincide with the expected ones after evacuation at 400°C (Fig. 4) shows that the intra-polyanion spin-spin interaction is not significant. Thus the losses of spin concentration at high reduction degree ($1 < x < 4$ are considered to arise from the inter-polyanion interaction. This conclusion was supported by the following experiments. The reduced samples with $x = 3.1$ and 3.8 were dissolved in water, and recrystallized after mixing with 10 times as much unreduced heteropoly acid. It was confirmed by ir that this procedure exerted no changes in internal states (oxidation states) of polyanions. Esr signals of the diluted samples after evacuation gave spin concentrations which coincided well with those expected from the reduction degrees. This shows that the inter-polyanion spin-spin relaxation was suppressed by dilution. Thus it is considered that, while the electrochemical reduction up to $x = 4$ produces 4 Mo^{5+} ions per anion, each Mo^{5+} ion is well separated from the others. As the Keggin anion is constructed by combining four Mo_3O_{13} units, it is likely that one electron is accomodated by each Mo_3O_{13} unit.

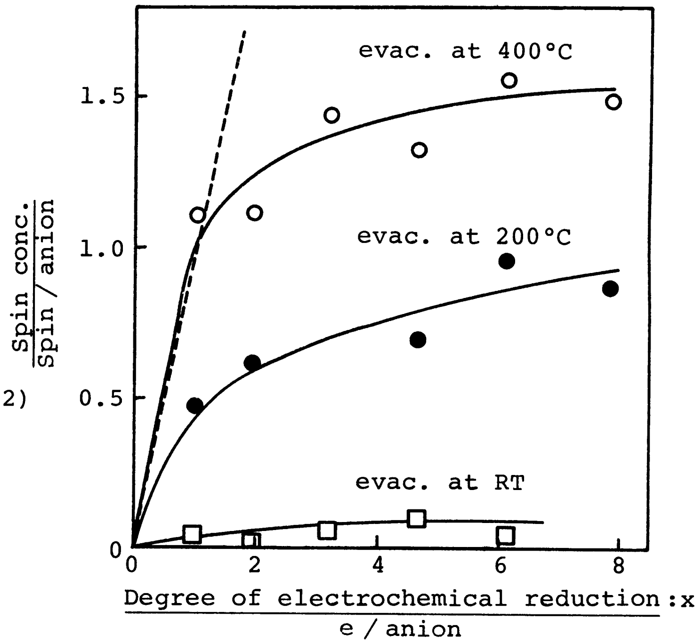

Fig. 4 Changes in the observed spin conc. with reduction degree of 12-molybdophosphoric acid evacuated at various temperatures.
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