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AN INFRARED STUDY OF THE REDUCTION OF TRIPOTASSIUM DODECAMOLYBDOPHOSPHATE WITH HYDROGEN

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Quantitative ir spectroscopic studies showed that the reduction of $K_3PMo_{12}O_{40}$ with H_2 in the early stage proceeded by consuming two bridging oxygens per Keggin anion. The process was accompanied by the stoichiometric formation of Mo^{5+} according to the XPS measurements. It was suggested that terminal oxygens were removed after two oxygens per Keggin anion were taken off.

Dodecamolybdophosphates are known as catalysts for the oxidation of methacrolein. Although a redox mechanism has been accepted for the catalysis,[1,2] little is known about the real nature of the redox process. In this report, we tried to elucidate the reduction process of $K_3PMo_{12}O_{40}$ in contact with hydrogen by using ir and XPS spectroscopic techniques.

The sample dodecamolybdophosphate ($K_3PMo_{12}O_{40}$) is thermally stable up to 650°C.[3] It was prepared from $H_3PMo_{12}O_{40}$ and K_2CO_3 according to the conventional procedure and calcined at 320°C for 2 h. The reduction with H_2 (30 torr) was carried out in a vacuum system in the temperature range 350-400°C for 3-50 h. The degree of reduction was monitored with an electrobalance (Cahn, type RG) connected to the apparatus. The water formed during reduction was removed with a dry ice-EtOH trap and completely evacuated after reduction. The reduced samples showed no weight decreases on heating up to ca. 500°C in vacuo. This excludes a possibility that a part of H_2 is present in the sample as H^+ after the reduction, as observed in the reduction of $H_3PMo_{12}O_{40}$ with H_2.[2] The reduced samples were scarcely reoxidized in dry air at room temperature. X-ray diffraction analyses confirmed that the samples maintained the same crystal structure before and after the reduction. Infrared spectra were recorded at room temperature using the KBr method. XPS spectra were recorded with Al Kα radiation. Binding energies were referenced to the $Au4f_{7/2}$ (83.8 eV) signal of evaporated gold.

The changes of ir spectra with a progress in reduction are shown in Fig. 1, where the reduction degree, Y, is defined as the number of consumed oxygen atoms per Keggin anion. The Keggin anion holds, in its fully oxidized form, three bonding types of oxygen, i.e., O bonded to P^{5+}(O_p), O bonded to two Mo^{6+}(O_b), and O bonded to a single Mo^{6+}(O_t). The ir spectrum (a) with $Y = 0$ is assigned as $\nu(P\text{-}O_p)$ 1065 cm^{-1} (O_p band), $\nu(Mo\text{-}O_b\text{-}Mo)$ 800 and 870 cm^{-1} (O_b bands), and $\nu(Mo\text{-}O_t)$ 960 cm^{-1} (O_t band), according to the literature.[4)] With a progress in reduction ((b) ~ (e)), the O_p band and O_b bands decreased significantly, while the O_t band remained almost unchanged, as was already reported by other researchers.[1)] The effects of reduction rate were examined by changing reduction temperature between 350-420°C. The ir spectra were scarcely dependent on the reduction rate. One notices that the O_b bands are replaced by new bands at $Y \geq 2$, and that a shoulder (948 cm^{-1}) appears in the O_t band region. At $Y < 1$ and $Y > 3$, the shoulder was less visible because of an overlapping with the main band.

The absorbances at the characteristic wave numbers are plotted as a function of Y in Fig. 2. The absorbance of O_p band decreased quite linearly with Y, to ca. 10 % of the original value at $Y = 2.1$. Similar linear decreases were also observed for the O_b bands, for which no corrections were made for overlapping with the new bands stated before: the true absorbances of them should be much smaller at $Y = 2.1$.

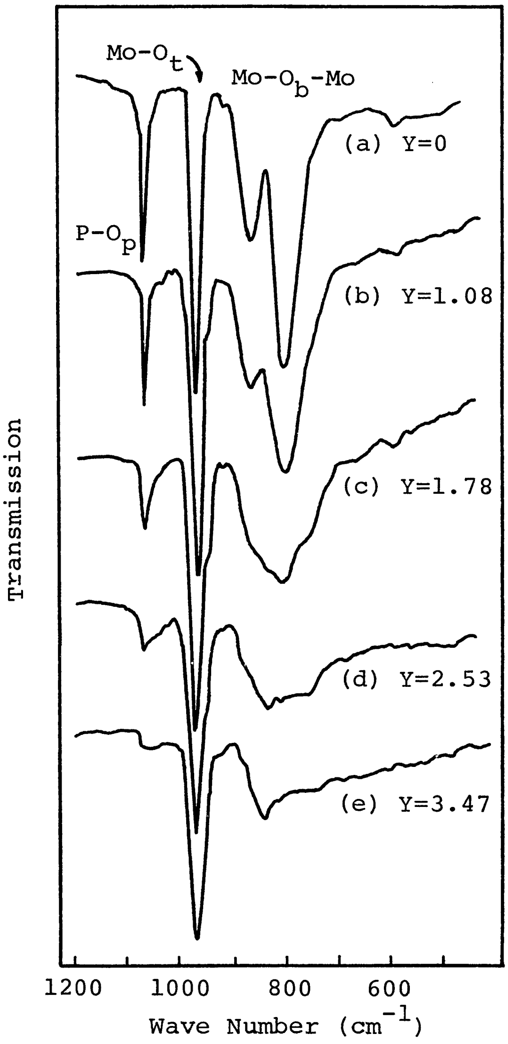


Fig. 1 IR spectra of tripotassium dodecamolybdophosphates at various degrees of reduction with H_2, $K_3PMo_{12}O_{40-Y}$.

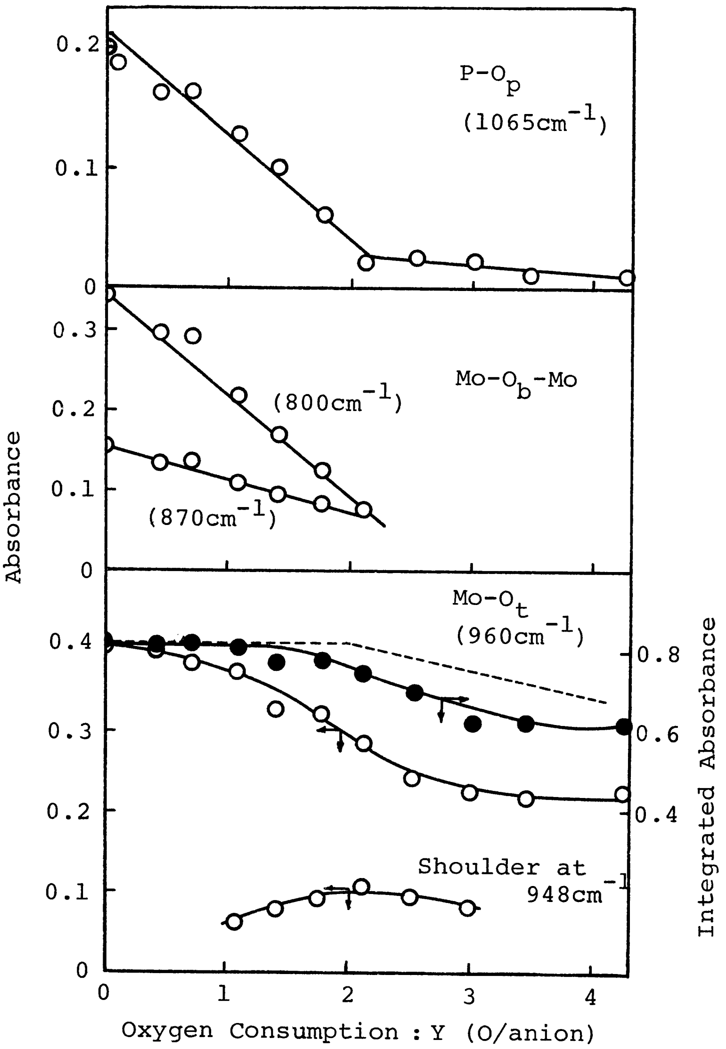


Fig. 2 Changes in the ir band intensities of heteropoly anion with reduction degree.

In contrast, the absorbance at 960 cm^{-1} for the O_t band decreased only gradually, being accompanied by the growth of the shoulder at 948 cm^{-1}. Both the O_t band and its shoulder being summed up, the integrated absorbance remained almost constant in the early stage of reduction ($Y < 1.5$). The linear decreases of the O_p and O_b bands up to $Y = 2$ show that each Keggin unit loses two oxygen atoms in this region, that is, the sample at $Y \leq 2$ consists of $K_3PMo_{12}O_{40}$ and $K_3PMo_{12}O_{38}$. We assume that the O_p and O_b bands, characteristic of the unreduced anion $(PMo_{12}O_{40})^{3-}$, are sensitive to the anion symmetry and disappear when the symmetry is changed by the removal of two oxygen atoms. On the other hand, the O_t band is considered to be little affected by the anion symmetry; its intensity will reflect the concentration of O_t atoms. The observed constancy of the integrated absorbance for the O_t band region at $Y < 1.5$ thus suggests that the O_t atoms are preserved, only a part of them shifting to the shoulder position (948 cm^{-1}). We consider that the shoulder is assigned to the terminal oxygen bonded to a pentavalent molybdenum atom. Based on these consideration, it seems quite probable that two O_b atoms are removed per Keggin unit at $Y < 2$. The participation of O_b was previously proposed for the reduction of $Ag_3PMo_{12}O_{40}$ with H_2[1)] by Tsuneki et al. At $Y > 2$, the integrated intensity for the O_t band region tends to decrease as stated before. The slope of the decrease is roughly equal to 1/12, suggesting that the O_t atoms are reactive in this stage. It is noted that the O_p and O_b bands remain partly at $Y > 2$. Probably this is because the reduction accompanies some extent of heterogeneity.

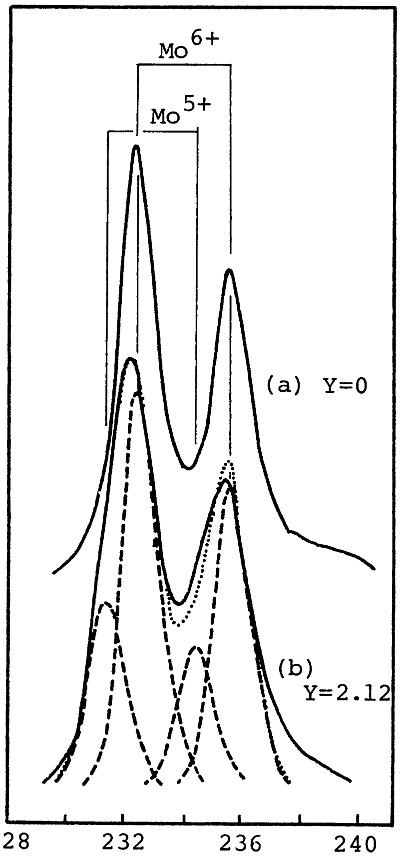
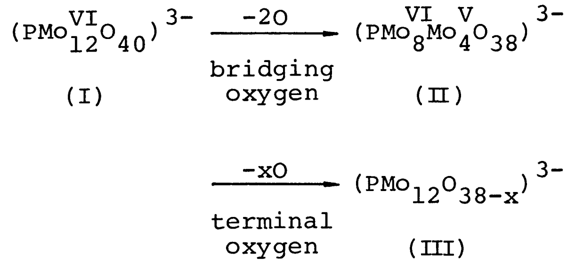


Fig. 3 XPS spectra of $K_3PMo_{12}O_{40-Y}$ (a) before and (b) after the reduction with H_2 (solid lines). Broken and dotted lines represent deconvoluted and synthesized curves, respectively.

In conjunction with the above ir study, the valence states of the metal cations were examined by XPS. The binding energy (BE) of P2p was 133.4 eV for both reduced and unreduced samples, confirming that the valence state of P^{5+} is kept during reduction. The spectrum of Mo3d region consists of a doublet of $Mo3d_{3/2}$ and $Mo3d_{5/2}$ as shown in Fig. 3(a). The BE values of these two levels for unreduced $K_3PMo_{12}O_{40}$ were 235.5 and 232.4 eV, respectively, in good agreement with those reported for $H_3PMo_{12}O_{40}$.[5)] In the reduced samples, each signal became broader with a slight shoulder appearing on the lower BE side (Fig. 3(b)). Spectrum deconvolution revealed that these shoulders corresponded to a doublet for pentavalent Mo ions, i.e., $Mo^{5+}3d_{3/2}$ (234.4 eV) and $Mo^{5+}3d_{5/2}$ (231.3 eV). The formation of Mo^{4+} was detected only when the sample was reduced extensively, e.g., up to $Y = 4.27$. Fig. 4 shows the fraction of Mo^{5+} in total Mo, $Mo^{5+}/(Mo^{5+} + Mo^{6+})$, deduced from the XPS intensities, as a function of Y. The observed Mo^{5+} fractions are in good agreement with those calculated on the assumption that the removal of an oxygen atom produces two Mo^{5+} ions. This confirms that only Mo^{5+} ions are produced stoichiometrically at $Y < 2$.

On the basis of these results, we conclude that the reduction of $K_3PMo_{12}O_{40}$ with H_2 proceeds as follows.



$$(\mathrm{PMo}^{\mathrm{VI}}_{12}\mathrm{O}_{40})^{3-} \xrightarrow[\text{bridging oxygen}]{-2\mathrm{O}} (\mathrm{PMo}^{\mathrm{VI}}_{8}\mathrm{Mo}^{\mathrm{V}}_{4}\mathrm{O}_{38})^{3-}$$

(I) (II)

$$\xrightarrow[\text{terminal oxygen}]{-x\mathrm{O}} (\mathrm{PMo}_{12}\mathrm{O}_{38-x})^{3-}$$

(III)

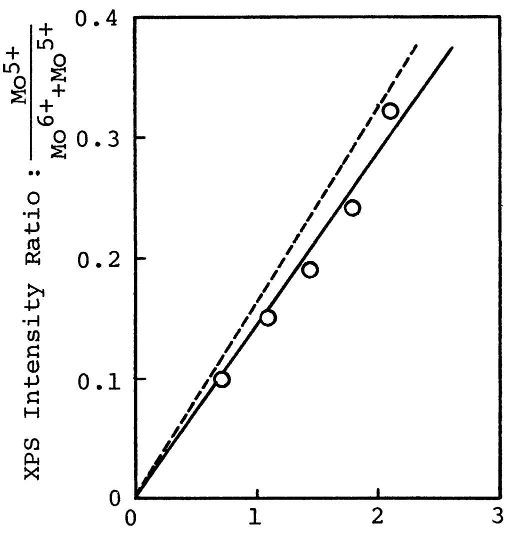


Fig. 4 Correlation between the surface Mo^{5+} fraction and degree of reduction.

Broken line represents the Mo^{5+} fraction expected from Y.

In the earlier stage of $Y \leq 2$ two oxygen atoms, most likely bridging oxygen, are deprived from each Keggin unit to form a mixture of (I) and (II). In the later stage of $Y > 2$ terminal oxygen seems to participate in the reaction. It was reported that the electrochemical reduction of the Keggin anion was initiated by two electron reduction,$^{6)}$ in contrast to the four electron reduction in the present case. The apparent difference is understandable if one considers that H_2 is a rather strong reductant capable of eight electron reduction.

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