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# REDOX PROPERTIES OF TRISILVER DODECAMOLYBDOPHOSPHATE CATALYST

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Redox properties of $Ag_3PMo_{12}O_{40}$ were studied by means of IR spectroscopy combined with $^{18}O$-tracer technique. Oxygen of inner core oxy-anion, $PO_4^{3-}$, were not removed by reduction with $H_2$, although IR spectra due to $PO_4^{3-}$ drastically changed. Exchange of terminal and bridge-bonded oxygen was so fast under the condtion employed here that all the oxygens equally participated for the redox cycles of the compound.

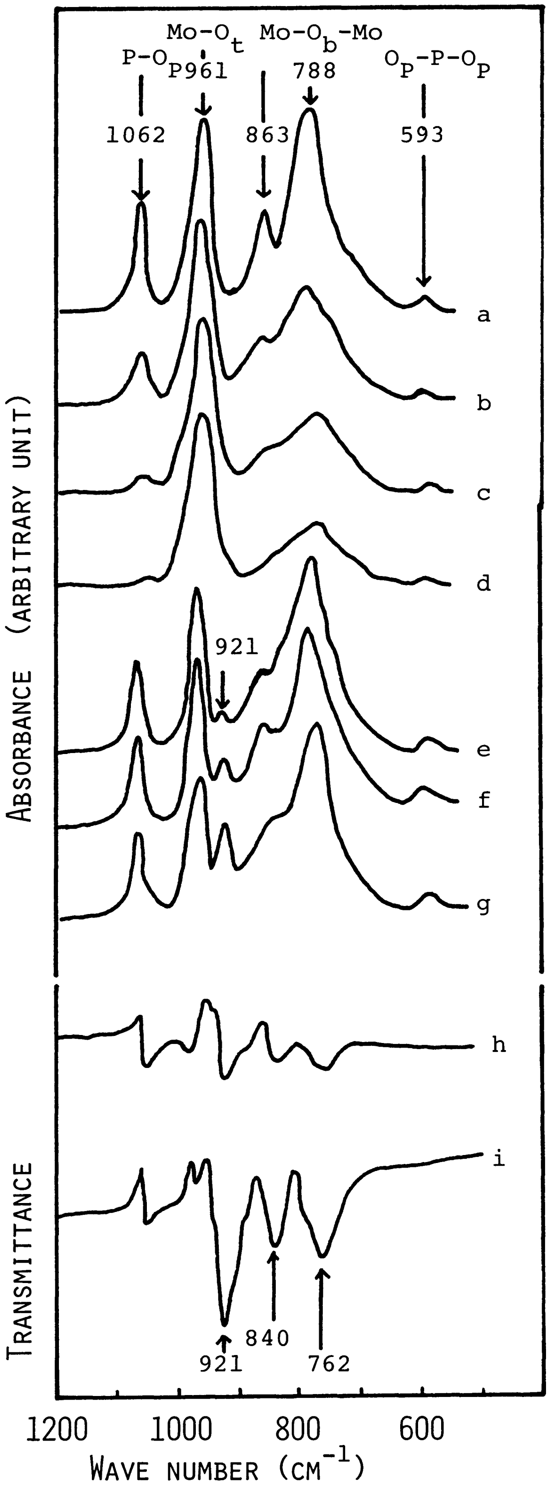
Dodecamolybdophosphoric acid ($H_3PMo_{12}O_{40}$) and its salts are one of the well known heteropoly compounds. Such compounds have high oxidation activity and strong acidic nature as well.[1)] Hence, their behaviors as catalysts are of stimulated interest both from scientific and practical point of view. X-ray[2)] IR and Raman studies[3)] has revealed that the anion, known as "Keggin structure", has three kinds of oxygens: (1) Twelve terminal oxygens, $O_t$, which locate at outermost positions of the anion and each of them attaches to one Mo atom, (2) twenty four bridge type oxygens, $O_b$, each of which binds to two Mo atoms, and (3) four oxygens of inner core oxy-anion, $O_p$. The latest one also coordinates to three Mo atoms through which outer shell of $Mo_3O_{12}$ sub unit is linked to hetero atom, P.[2)]

Our objective in this report is to clarify what kind of oxygen in the anion plays a role in redox cycles of the compounds: Which oxygen is taken away upon reduction and how the anion structure is regenerated upon oxidation. Among several transition metal salts of the polyacids, Ag-salt was found to be most readily[4)] reduced with hydrogen and, hence, chosen as a test material.

Heteropolyacid was prepared by the standard procedure.[5)] Ag-salt was prepared by the reaction of silver carbonate with the acid. The reduction with $H_2$ and oxidation with $^{18}O_2$ (99% $^{18}O$) were done using closed gas-circulation apparatus. The changes after such redox cycles were pursued by IR spectroscopic method. Spectra were recorded with Hitachi EPI-G3 spectrometer. KBr pellet method was employed for the spectroscopic measurements. Grinding with KBr, pelleting and spectroscopic measurements were done in atmosphere of air. Oxidation of reduced sample and oxygen exchange between the sample and atmospheric air during the procedure was insignificant, because it was confirmed that IR spectrum of reduced sample and $^{18}O$-exchanged one did not change appreciably after prolonged (several weeks) contact with atmospheric air.

IR spectrum of $Ag_3PMo_{12}O_{40}$ was given in Fig.1, curve a, in which assignments of these peaks given by Rocchiccioli-Deltcheff et.al.[3)] were also noted. The bands are all due to anion structure. Curves b, c and d are the spectra of partially reduced samples whose degree of reduction increase in alphabetical order. For the preparation of the reduced samples, TPR (Temperature Programmed Reduction) apparatus was employed[4)]: The reduction was done with $H_2$ (5.72%)-$N_2$ (balance) flow at temperatures increasing with a constant rate (10°C/min) and the $H_2$-consumption was continuously monitored by T.C. cell. The consumption of $H_2$ takes place 150 ~ 300°C, and the reduction was stopped at the time when the comsumption of $H_2$ corresponds to 0.8, 2.3, and 3.0 oxygen(s) per anion respectively. It should be noted that the same spectrum as curve d was obtained when the reduction was done in a closed gas-circulation apparatus at 200°C with $H_2$ pressure of 150 Torr, provided that the degree of reduction was the same as that for curve d. Intensities of the peaks due to $\nu[P\text{-}O_p]$, $\delta[O_p\text{-}P\text{-}O_p]$ and $\nu[Mo\text{-}O_b\text{-}Mo]$ drastically decreased with the degree of reduction while the one due to $\nu[Mo\text{-}O_t]$ did not change (peak height decreased while width increased). At first glance it seems likely that both $O_p$ and $O_b$ are removed while $O_t$ remains. However the situation is far more complicated than expected from such a simple view.

Curves e, f and g show the spectra after several $H_2$ reduction-$^{18}O_2$ oxidation cycles, e the first, f the second and g the sixth cycle respectively. In each reduction procedure, the reduction was stopped at the time when three oxygens per one anion had reacted with $H_2$. It was confirmed that



Samples: a; reference, b - d; partially reduced samples whose degree of reduction were 0.8, 2.3, and 3.0 oxygens per anion respectively, e - g; after first, second and sixth redox cycles respectively (reduction at 200°C with 150 Torr of $H_2$ and oxidation at 300°C with 50 Torr of $O_2$), h,i; samples e and g with reference beam attenuated with sample a.

simple exchange of gaseous $^{18}O_2$ and oxygen of the solid did not takpe place. Accordingly, introduction of $^{18}O$ into solid phase occurs solely through redox cycles: $^{16}O$ is taken away upon the reduction and $^{18}O$ is introduced upon the oxidation.

It was found that $\nu[P\text{-}O_p]$, which had disappeared, regenerated upon $^{18}O_2$ oxidation. However, isotope shift was hardly observed. The shift of $[P\text{-}O_p]$ after the sixth cycle was but 2-3cm$^{-1}$, which was too small to account for the formation of $[P^{16}O_{4-x},{}^{18}O_x]^{3-}$. It is noteworthy that 36% of oxygen of the total is replaced by $^{18}O$ after the sixth cycle.[6)] Tentative explanation for the disappearance and regeneration of $\nu[P\text{-}O_p]$ is as follows. $O_p$, which has bound to P, belongs to outer shell after the reduction in order to compensate excess charge on Mo atoms. Since no bonding nature between $O_p$ and P remains after the reduction, IR band due to $\nu[P\text{-}O_p]$ disappears. When outer shell is reoxidized, $O_p$ binds to P again. During the redox cycle, no isotope exchange is necessary to occur. The small shift, 2-3cm$^{-1}$, is due to change of total mass of anion, which is due to replacement of $^{18}O$ with $^{16}O_b$ and/or $^{16}O_t$.

New peak at 921 cm$^{-1}$ in the spectra e, f and g was assigned to $\nu[Mo\text{-}^{18}O_t]$. Over-all picture of the region, 970-700 cm$^{-1}$, also significantly changed. In order to show the isotope shift more clearly, reference beam of spectrometer was attenuated by the sample a. The results are shown in the same figure, curves h and i, however vertical axis for the two curves is transmittance instead of absorbance. It is apparent that $^{18}O$ was introduced in place of $O_b$ and $O_t$. The isotope shift $\Delta\nu[Mo\text{-}O_t]$ and $\Delta\nu[Mo\text{-}O_b\text{-}Mo]$, lay in reasonable order of magnitude.

Since $O_t$ is not removed by the reduction, it is likely that mixing of $O_t$ and $O_b$ takes place during the redox cycles. Following calculations showed that the rate of mixing was extremely high. Let n be the number of redox cycles, $X_n$ be the fraction of $^{18}O$ after nth cycle and suppose that complete mixing of $O_t$ and $O_b$ is established,

$$X_n = 0.99[1-(33/36)^n] \qquad (1)$$

In the formulation, following values were taken into consideration: Atomic fraction of $^{18}O$ in gaseous oxygen to be 0.99, number of replaced oxygen per one anion per one redox cycle to be 3 and number of oxygen, $O_b$ and $O_t$ but excludes $O_p$, to be 36. On

Table 1 Change in Fraction of $^{18}O$ in Terminal Oxygen after Several Redox Cycles

| Number of redox cycles | Fraction of $^{18}O$, $X_n$ | |
|---|---|---|
| | Observed by IR (Eq. 2) | Calculated based on complete mixing (Eq.1) |
| 1 | 0.097 | 0.083 |
| 2 | 0.19 | 0.16 |
| 6 | 0.39 | 0.40 |

Sample; $Ag_3PMo_{12}O_{40}$, Reduction; with 150 Torr of $H_2$ at 200°C for 10 min, Oxidation; with 50 Torr of $^{18}O_2$ at 300°C for 2 hr.

the other hand, the fraction of $^{18}O$ in terminal oxygen is calculated from experimentally obtained spectra by the use of Eq. (2).

$$X_n = [I_{921}/(I_{961} + I_{921})]_n \qquad (2)$$

Herein, I is integral intensity and subscripts are the wave numbers at which IR bands appear. Calculated values by the use of Eqs. 1 and 2 were listed in Table 1. Agreements were fairly good, indicating the complete mixing assumption was valid.

We have tacitly assumed so far that all anions, either on surface layer or in bulk phase, equally participate in redox cycles. The assumption seems reasonable because the amount of hydrogen consumed was so large while surface area was small (ca. 1 $m^2/g$). The results given in Table 1 also supports the view: If the redox cycle takes place solely on surface layer, introduced $^{18}O$ in the first oxidation process predominantly removed upon the second reduction process. This means that $X_n$ does not change a lot with number of redox cycles but stays at constant and low level (roughly speaking, the fraction of surface molecule to the total). This apparently is not the case.

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6) Calculated based on the complete mixing of all the oxygens, $O_b$, $O_t$ and $O_p$. Method of calculation is given in the later section of the text.

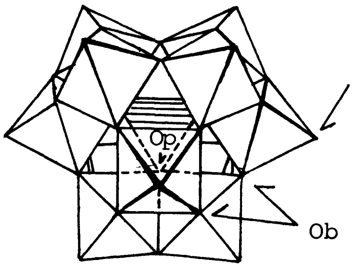

Fig. 2 "Keggin structure" of $[PMo_{12}O_{40}]^{3-}$.

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