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BEHAVIORS OF LATTICE OXYGEN OF TRISILVER DODECAMOLYBDOPHOSPHATE CATALYST IN THE REACTION OF H_2 + $^{18}O_2$

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Behaviors of lattice oxygen of $Ag_3PMo_{12}O_{40}$ in catalytic reaction of H_2 + $^{18}O_2$ were studied. ^{18}O was predominantly introduced in place of bridge-bonded oxygen of polyanion, ($PMo_{12}O_{40}{}^{3-}$). Presumably, the reaction proceeds through redox cycles of bridge-bonded oxygen.

In the previous report$^{1)}$, we studied the behavior of oxygen in $Ag_3PMo_{12}O_{40}$ catalyst when it was subjected to H_2-reduction followed by $^{18}O_2$-oxidation cycles. There are three kinds of oxygen in the anion; terminal oxygen (O_t), bridge-bonded one (O_b) and oxygen of inner core oxyanion, $PO_4{}^{3-}$ (O_p). The location of these oxygen in the anion was described in the previous paper$^{1)}$. Isotope exchange between gaseous $^{18}O_2$ and ^{16}O in the lattice did not occur, however, upon H_2-reduction followed by $^{18}O_2$-oxidation cycles, ^{18}O was introduced in place of O_b and O_t. It seemed that all the O_b and O_t, either on the surface or in bulk phase, were replaced with ^{18}O in equal probability.

Hence bonding natures of O_b and O_t are significantly different with each other, it seems unlikely that both oxygen equally participate in redox cycles. The apparent equal participation is rather due to fast mixing of O_b and O_t in the solid phase. In the reduction-oxidation cycles, which were employed in the previous studies, the reduction of the catalyst proceeds to a considerable extent, which makes remaining oxygen mobile.

The objective of this paper is to determine which oxygen predominantly plays a role in catalytic cycles. To do this, the reaction of H_2 + $^{18}O_2$ was done in an excess $^{18}O_2$ region, in order that the catalyst stays in an oxidized form. Also the lower temperature was employed for the reaction.

The catalyst was prepared by the method described before$^{1)}$. It was outgassed at 300°C for 1 hr prior to the reaction in order to remove sorbed water. The weight of employed catalyst, excluding sorbed water, was determined with DTA-TG analysis of the sample of the same lot. After the in situ pretreatments, the reaction of H_2 + $^{18}O_2$ was done at 150°C until hydrogen was depleted. It took 6 and 4 hr for runs 1 and 2 respectively. Initial pressures of H_2 and $^{18}O_2$ were 73 and 45 Torr for the run 1 and 91 and 63 Torr for the run 2. Weight of the employed catalyst was 19 and 100 mg for the runs 1 and 2 respectively. Since the ratio of initial pressures

$H_2/^{18}O_2$ is smaller than 2, the gas phase composition gradually approaches to an oxygen-rich region as the reaction proceeds. Total amounts of reacted oxygen were 1.11 and 1.60 mg-atom for the runs 1 and 2 respectively, which corresponds 3.34 and 0.915 times the amount of oxygen in the employed catalyst (based on 40 oxygens per one anion).

IR spectra of the catalyst was measured with the previously described method[1]. The catalyst after or before the use for the reaction were subjected to IR spectroscopy by means of KBr pellet method. Raman spectra was recorded with the use of Nihon Denshi JPG 4000 spectrometer, with Ar laser of 514.527 nm as a light source. A powder method was employed for the measurements in order to avoid potential exchange of oxygen of solid phase with the solvent.

IR spectra of the catalyst after the reaction were given in Fig.1. It was found that the catalyst was slightly reduced after the use for the run 1. Such reduction was not found for the run 2, because the catalyst had been kept in atmosphere of remaining $^{18}O_2$ for 2 hr at the same temperature. In order to show the effect of isotope replacement more clearly, spectra of reference samples, which did not contain ^{18}O and had been reduced to the same extent, were superimposed in the figure. Comparison of solid and dotted lines shows that ^{18}O is introduced in place of O_b to a considerable extent. To a lesser extent, on the contrary, ^{18}O is incorporated in place of O_t (a rough calculation showed 20 % of O_t was replaced by ^{18}O). The behavior of O_p was the same as reported previously: No isotope replacement was observed. When the catalyst was heated to 300°C in atmosphere of air, spectra b and d were obtained. It should be noted that oxygen exchange between O_b and O_t occurs at the temperature[1]. The comparison (a vs. b, c vs. d) shows that the concentration of ^{18}O in place of O_t increase after the calcination. Hence, the concentration potential of ^{18}O had been higher at O_b after the reaction.

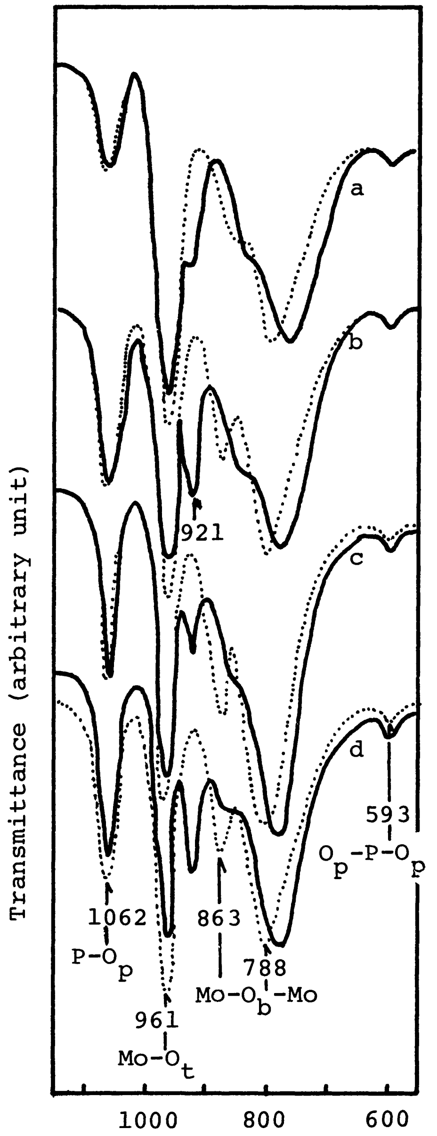


Fig. 1 IR spectra of $Ag_3PMo_{12}O_{40}$ after the use for the reaction, $H_2+^{18}O_2$. a, c; run 1 and 2 respectively, b,d; run 1 and 2 followed by calcination at 300°C for 1 hr. Dotted lines are the references.

It can be more clearly shown by Raman spectroscopy because Raman shift due to ν(Mo-O_b-Mo) appears without any interference of other peaks while two broad bands due to ν(Mo-O_b-Mo) appear in the vicinity in IR spectroscopy. Fig. 2 shows Raman spectra of the catalyst before and after the use for run 2. ν(Mo-O_b-Mo) which had appeared at 880 and 605 cm^{-1} almost completely shifted to 860 and 590 cm^{-1}, indicating $^{16}O_b$ was replaced by ^{18}O. On the other hand ν(Mo-O_t) still remained to a considerable extent.

We shall discuss here the mechanism of the reaction, H_2 + O_2; whether it proceeds through redox cycles of the catalyst (redox mechanism) or through direct coupling of adsorbed oxygen with hydrogen (Langmuir-Hinshelwood mechanism). In the former mechanism, the catalytic reaction accompanies the isotope replacement of lattice oxygen while it is not necessary to occur in the latter mechanism. The experimental findings that most of O_b was replaced by ^{18}O strongly suggests that the reaction is of redox type. Following calculation will give an additional support for this. If the reaction proceeds through redox cycles of O_b, with an additional assumption that the mixing of O_b in solid phase is fast in comparison with the surface reaction, it follows that2),

$$\int_0^t r\,dt = N \ln \frac{1}{0.99-X} \qquad (1)$$

where x is fraction of ^{18}O in total O_b, r is rate of reaction and N is total number (including both surface and bulk) of O_b. 0.99 is ^{18}O fraction of the reactant oxygen. Since we know the value of $\int_0^t r\,dt$ which corresponds to the total amount of reacted oxygen atom by the time t (36.6 atoms per anion after the completion of run 2) and N is 24 atoms per anion, we have x = 0.78. If either one of the assumptions is invalid, x will be smaller than the above calculated value. Apparently fraction of ^{18}O at O_b, x in eq. (1), is very high as shown in Fig. 2, indicating <u>both</u> assumptions are valid. The redox mechanism is also supported by experimental findings that the rate of catalytic reaction of $H_2 + O_2$, the rate of reduction of the catalyst with H_2 and the rate of oxidation of the reduced catalyst, all lies in the same order of the magnitude4).

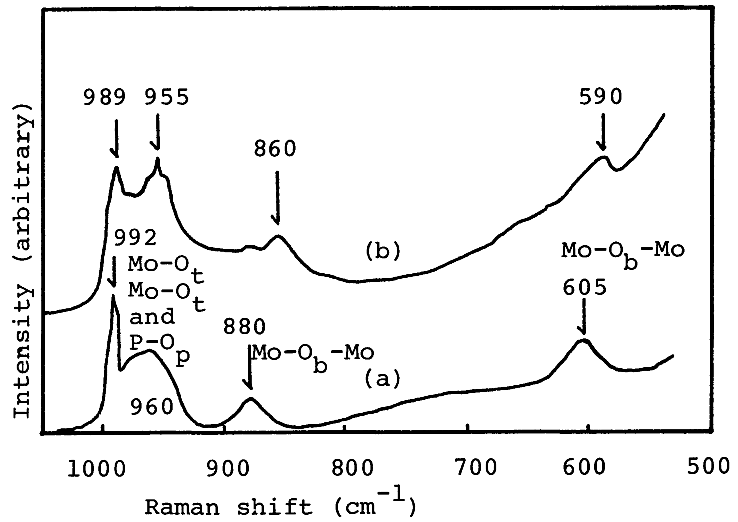
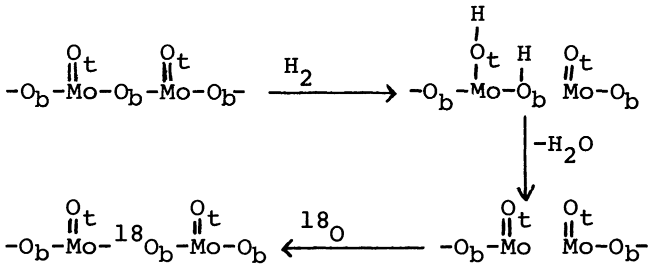


Fig. 2 Raman spectra of the catalysts, before (a) and after (b) the use for the run 2. Assignments of the peaks are given in ref. 6.

Accordingly, it can be concluded that the reaction proceeds through redox cycles of the bridge bonded oxygen. Also the mixing of O_b in the solid phase is extremely fast in comparison with the surface reaction.

It is has been proposed5) that the reduction of MoO_3 proceeds through rearrangement of the initially corner-linked MoO_6 octahedra into an edge-linked octahedra, resulting in a shear plane, in which double bonded oxygen does not participate. Our findings may be related to the view. It should be borne in mind, however, that the possibility of the participation of O_t for certain elementary steps still remain. For example, our experimental findings may be explained by the following set of steps, where O_t also participates in the catalytic sequence.



What we can say with certainty at the present time is that the bridge bonded oxygen is taken away and gaseous oxygen is incorporated at the position.

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References and Note

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