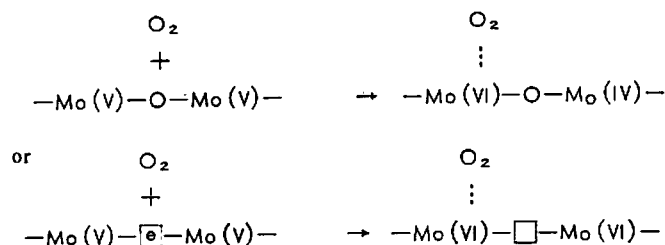# ESR STUDIES OF THE HEXAGONAL HYDRATE OF MOLYBDENUM OXIDE

AND ITS CHANGES ON TREATMENTS

IN VACUO AND IN HYDROGEN

BY NORIYUKI SOTANI

The hexagonal hydrate of molybdenum trioxide and its change on treatments in *vacuo* and in hydrogen were studied by ESR spectroscopy. The hydrate gave no ESR signal, but the signal due to Mo(V) appeared in the case of the reduction of hexagonal MoO_3 and rhombic MoO_3. Mo(V) was formed in oxygen deficient MoO_3 as a defect during the reduction. The signal intensity changed according to the degree of the reduction. The intensity of the reduced sample decreased when oxygen was added and recovered its value by evacuation. This means that O_2 molecule adsorbs weakly on Mo(V). The mechanism of the change in intensity by oxygen adsorption and desorption is assumed as follows:

$$\begin{array}{ccc}
O_2 & & O_2 \\
+ & & \vdots \\
-Mo(V)-O-Mo(V)- & \longrightarrow & -Mo(VI)-O-Mo(IV)-
\end{array}$$

$$\text{or} \quad \begin{array}{ccc}
O_2 & & O_2 \\
+ & & \vdots \\
-Mo(V)-\boxed{\odot}-Mo(V)- & \longrightarrow & -Mo(VI)-\square-Mo(VI)-
\end{array}$$

Introduction

There are many ESR works of MoO_3[1,2], MoO_3 supported on Al_2O_3[3-5] or SiO_2[6,7] and molybdate catalyst[7-11], in order to know the correlation between Mo(V) in molybdenum oxide and its catalytic

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activity. The signals, which were assigned to Mo(V), were observed on supported molybdenum oxide[3-7] and binary catalyst[7-9], but, on the unsupported molybdenum oxide, any signal due to Mo(V) was not observed at room temperature[1,2]. Therefore, it was assumed that the supporters or the constituents in binary catalysts stabilized the Mo(V) state. However, Cornaz *et al.*[1] detected the signal due to Mo(V) at −195°C on single MoO_3 sample.

The author[12] obtained the hexagonal hydrate of molybdenum trioxide, a new form of the hydrate of molybdenum trioxide, in his studies on the molybdenum oxides and the hydrates. The properties and the behaviors of the hexagonal hydrate on the treatments in *vacuo*, in hydrogen and in the hydrogen-thiophene mixture at various temperatures were studied by means of X-ray diffraction analysis, IR spectroscopy and DTA-TGA. In these studies, the author made clear the compositional and structural changes of the hexagonal hydrate due to dehydration, transformation, reduction and sulfurization, accompanied by these treatments.

In these reactions, Mo(V) is expected to be formed, even though any evidence of Mo(V) compounds was not obtained. In connection with the previous work[12], the author studied, by ESR spectroscopy, the sample and its change of the state resulted from the treatments in *vacuo*, in air and in hydrogen, with the purpose of revealing the role of Mo(V) in the change of the state of the hydrate.

Experimental

Sample

The hexagonal hydrate of molybdenum trioxide was prepared by the same method as has been previously described[13].

ESR measurements

The ESR measurements were performed on a JES 3BX Type (JAPAN ELECTRON OPTICS LAB.) spectrophotometer operating at 9.4 KMHz. The magnetic field was modulated by 100 KHz, and the first derivative of the spectrum was recorded. The peak-to-peak modulation amplitudes from 3 to 5 gauss were used in recording the spectrum.

The sample tubes were made of quartz of 5 mm in o. d. and 4 mm in i. d. The tube had a stop cock and could be evacuated by connecting it to a conventional vacuum system with a ground glass joint. The samples were subjected to ESR analysis at room temperature after evacuation for 30 min under a vacuum of 10^{-4}–10^{-5} torr. The amounts of the sample used for ESR measurements were 4 to 40 mg. Within this range, the signal intensity increased in exact proportion to the sample weight. Intensities were calibrated by using one of the intensity of the lines from Mn^{2+} sample.

X-ray studies

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The precise method of X-ray diffraction analysis was described previously[13].

Experimental procedure

(1)   Heat treatment in *vacuo*. The hydrate sample was treated at 350° and 400°C under the vacuum of 10^{-4}–10^{-5} torr for 30 min.

(2)   Reduction. Reduction experiments were performed both in the closed system and in the flow system. In the experiments in the closed system, the hydrate sample was packed in the sample tube. After the evacuation at room temperature for 30 min under the vacuum of 10^{-4}–10^{-5} torr, the sample was reduced by the hydrogen purified by passing through the platinum catalyst and molecular sieves. After the reduction, the sample was subjected to ESR analysis. On the other hand, the hydrate sample was reduced in the flow system by atmospheric hydrogen with the rate of 0.1 mol/hr. After the reduction, the sample was quickly transferred to the tube for ESR measurement, evacuated and subjected to ESR analysis.

Results

Treatment in *vacuo*

The hexagonal hydrate of molybdenum trioxide gave no ESR signal in air or in vacuum of 10^{-4}–10^{-5} torr at room temperature. Fig. 1 shows the spectra of the sample treated in *vacuo* for 30 min at 350° and 400°C. The signal with $g=1.934$ and $g=2.001$ was observed when the sample was treated at 350°C, though any structural change was not observed by X-ray diffraction analysis. It was reported[12] that the dehydration of the hydrate took place within 5 min at 350°C and the hydrate transformed to anhydrous hexagonal MoO_3 (denoted as (H)) by heating, without any change in structure. By treatment at 400°C, the g-values of the signal shifted to $g=1.925$ and $g=1.995$ (Fig. 1). By the X-ray studies, the sample was transformed to rhombic MoO_3 (denoted as (R)).
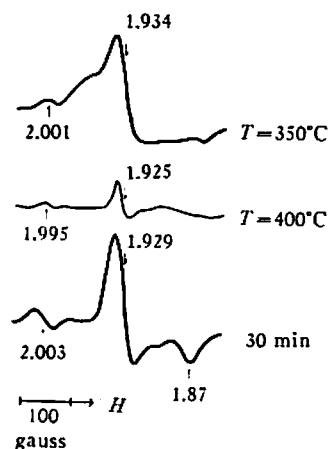

Fig. 1   The ESR spectra of the sample (A; $T=350°C$ in *vacuo*, B; $T=400°C$ in *vacuo*, C; reduced with hydrogen at 350°C for 30 min)

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Reduction of the sample

The hydrate sample was reduced by hydrogen of 28–31 torr at 350°C in the closed system and was subjected to ESR analysis after evacuation. The signal, similar to that of the sample obtained by heat treatment in *vacuo*, appeared by the 3 min reduction. Fig. 1 shows the spectrum of the sample reduced for 30 min. The line shape of the spectrum is asymmetric with a main signal with the g-value near 1.93 and a shoulder with $g=1.87$, showing the line shape of the nonoriented polycrystallines. The g-value of the main signal changes from 1.936 to 1.929 and the intensity increases with the progress of the reduction.

A small signal with $g=2.003$ was also observed.

According to X-ray diffraction analysis, the hydrate sample changed as follows: (H)→(R)→MoO_2 (denoted as (D)), when it was reduced with hydrogen at 350°C in the flow system. The composition of the reduced sample was a mixture of (H), (R) and (D), but the relative amounts of them varied according to the degree of the reduction. However, the reduction at 350°C was so slow that the hydrate sample was reduced with an atmospheric hydrogen at 400°C to obtain the further reduced sample. The composition of the sample was, at first, a mixture of (H), (R) and (D). By the 40 min reduction the composition changed to a mixture of (R) and (D), and by the 60 min reduction, most of (D), the final reduction product. The oxides of Mo(V) and Mo(III) states were not detected by X-ray diffraction analysis throughout these reduction experiments.

The ESR signal with $g=1.925_5$ and $g=1.996$ appeared in the 5 min reduction. The signal intensity of $g=1.925_5$ changed with the degree of the reduction. The intensity is plotted against the fraction of (D) in the sample as shown in Fig. 2. The intensity has a maximum at about 5% of (D) and gradually decreases to a very small value at about 60% of (D). The signal with $g=1.996$ also takes high intensity at low (D) content, but the intensity is not completely parallel to the main signal (Fig. 2).
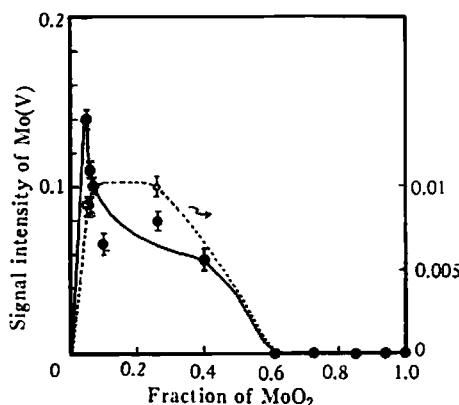

Fig. 2   The change in intensity of the fraction of MoO_2 in the sample reduced with hydrogen (●: $g=1.93$, ○; $g=2.00$)

Change in intensity of spectra of the reduced sample with the atmosphere

Fig. 3 shows the change in the intensities of the main signal (Curves A, B and C) and the signal with $g=2.00$ (Curves B′ and C′) with time, when the various atmospheres were added to the reduced sample. The curve A shows the change in intensity when the sample was evacuated immediately after

reduction. No change is observed. The curve B is the result when air was introduced after reduction. Intensity decreases to a certain minimum value by the 40 min exposure. The curve C shows the change in intensity when the sample was stood in reduction atmosphere without evacuation after the reduction and, then, treated as indicated in the figure. The first decrease seems to be due to the adsorption of H_2O produced by the reduction. The curve C also shows that the decrease and the increse in intensity by addition of air and by evacuation are reversible.
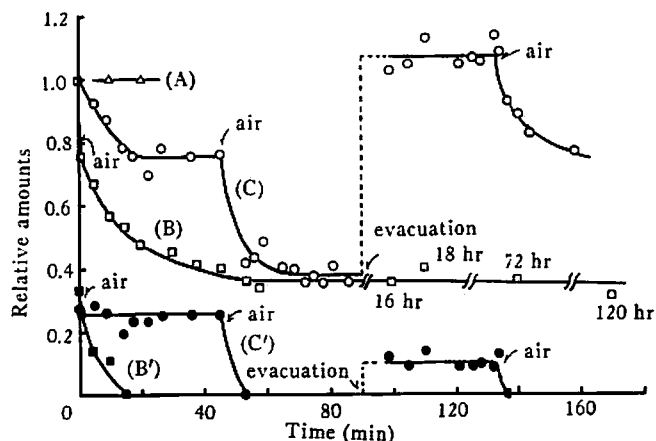

Fig. 3 The change in the signal intensity of the sample at various atmospheres

The signal with $g=2.00$ (Curves B' and C') changes parallel to the main signal. Any new signal attributable to adsorbed oxygen was not detected by addition of air.

Fig. 4 shows the change in the intensity of the signal, when the water vapor (18.6 torr) was added to the reduced sample. The intensity of the signal with $g=1.93$ rapidly decreases by the 5 min exposure and keeps a constant value for further exposure. At the same time, the signal with $g=2.00$ disappears by the 5 min exposure.
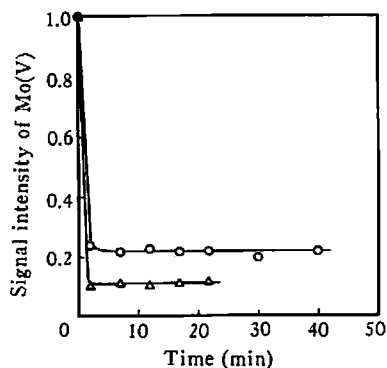

Fig. 4 The change in the signal intensity of the sample on the adsorption of water (○; reduced for 5 min, △; reduced for 10 min)
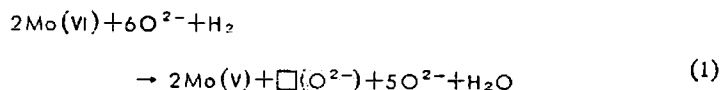
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Discussion

Molybdenum can exist in any of four valences $6+$, $5+$, $4+$ and $3+$. Hexavalent is diamagnetic and, therefore, gives no ESR signal. Tetravalent molybdenum, even if it were paramagnetic, was reported to be observed only at very low temperature[14]. Kihlborg reported[15] that no phase corresponding to the oxide, $MoO_{1.5}$, was observed, even though MoO_3 had been reduced by hydrogen at 500°C for a long period. In the present work, the final reduction state determined by X-ray diffraction analysis was (D) and the reduction temperature was lower than Kihlborg's reduction temperature. Therefore, the formation of Mo(III) can not be expected.

As for Mo(V), ESR spectra with $g=1.947$[16] and $g=1.950$[17] were observed for $(NH_4)_2MoOCl_5$ and $MoOCl_5^{2-}$ ion in HCl solution, respectively. Also for the supported molybdenum catalyst, the signal with g-values between 1.924 and 1.950 were reported by many workers and were attributed to Mo (V)[1-3, 7, 8, 10, 11, 13, 17]. Considering these previous works, it is reasonable to conclude that the main signal with the g-values near 1.93, obtained in this work, is attributed to Mo(V).
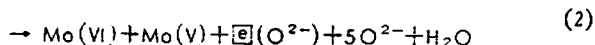
As described above, the samples treated in *vacuo* or reduced by hydrogen were composed of one or the mixture of (H), (R) and (D), and no other oxide was not detected. This fact shows that Mo(V) is contained in (H), in (R) or in (D). The signal intensity due to Mo(V) in the reduced sample shows a maximum at a few percent of (D) and decreases steeply with the progress of the reduction and reaches a very small value of about 60% of (D) as shown in Fig. 2. The above result shows that the signal is attributed to Mo(V) contained in (H) or in (R) phase.

It is interesting that the samples reduced to (D) by about 60% or more show only a very weak ESR adsorption due to Mo(V). (D) is well known to be a p-type semiconductor[18, 19]. These facts mean that the equilibrium concentrations of positive hole and of Mo(V) in (D) are not large. The fact that the signal intensity due to Mo(V) takes high value at very low (D) content seems to show that Mo(V) is formed as a super saturated state in (H) and in (R) at the early stage of the reduction, probably because of difficulty of the deposition as (D). The different results obtained by the previous works[1, 2] from the author's that Mo(V) was formed in MoO_3 probably came from the different reduction conditions.

Mo(V) in (H) or in (R) is formed by the following equations, accompanied by the formation of oxygen deficiencies or of the F-center;

$$2Mo(VI)+6O^{2-}+H_2$$

or

$$\rightarrow 2Mo(V)+\square(O^{2-})+5O^{2-}+H_2O \tag{1}$$

$$\rightarrow Mo(VI)+Mo(V)+\boxed{e}(O^{2-})+5O^{2-}+H_2O \tag{2}$$

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giving the n-type semiconductor. Slahelin *et al.*[20] and Kawaguchi[21] have reported that (R) is the n-type semiconductor. At the same time with the formation of Mo(V), the formation of the F-center is expected, according to the equation (2). The *g*-value of the F-center is expected to have a *g*-value close to that of free electron value of 2.0023, as known from the values obtained in alkali halides[22, 23]. The small signal with $g=2.003$ in the sample heated in *vacuo* and in hydrogen is assumed to be attributed to the F-center. Cornaz[1] also observed the signal with $g=1.943$ and 2.001 at $-195°C$, when MoO_3 was reduced by butene or treated under a vacuum of 10^{-4} torr, and proposed that the signal with $g=2.001$ was attributed to the F-center.

The measurements of the changes in intensity of the reduced sample (Fig. 3) show that Mo(V), produced by the reduction, disappears on adsorption of oxygen (Curve B and C) or water (Fig. 4), but it is reproducibly recovered by the evacuation at room temperature. The other part of Mo(V), however, is left unchanged by oxygen adsorption. The above facts show that a part of Mo(V) is situated in the bulk, and the other part on the surface or in the layer close to the surface disappears by oxygen adsorption. The F-center is also situated on the surface or in the layer close to the surface and disappears by oxygen adsorption. The reversibility of the changes in intensity shows that the deficiencies in the crystal remain unaffected by oxygen adsorption and, at the same time, shows that the adsorption of oxygen is very weak.

If the disappearance of Mo(V) by the adsorption of oxygen resulted from the electron transfer from adsorbed oxygen to Mo(V), the formation of O^- [24-26], O_2^- [27, 28], O_3^- [28, 30], O_2^{2-} [1] or O^{2-} is expected. O^-, O_2^- or O_3^- must show a new signal, but such a new adsorption did not appear in ESR spectra. Kazansky *et al.*[31] reported that the signal due to Mo(V) in MoO_3 supported on SiO_2 decreased by oxygen adsorption and new triplet signal with $g_1=2.018$, $g_2=2.010$ and $g_3=2.004$ was observed and assigned it to O_2^- anion-radical. On the other hand, Cornaz[1] observed on unsupported MoO_3 the decrease in intensity of the signal due to Mo(V) by the adsorption of oxygen and did not observe any new signal, which agreed with the author's result and he proposed the doubly bonded model of O_2^{2-} ion. Such inconsistency may be based on the difference of the samples, that is, supported and unsupported MoO_3. However, according to the author's experiments, oxygen adsorbs weakly and reversibly desorbs by evacuation at room temperature. These facts mean that oxygen adsorbs as O_2 molecule and interacts weakly with the substances. Therefore, Mo(V) will disappear by the electron transfer from one Mo(V) or from the F-center to another Mo(V), because of the increase in the instability of Mo(V)

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state induced by the adsorption of oxygen. It is well known that O_2 molecule is paramagnetic[32, 33],
but adsorbed oxygen does not show any signal. O_2 molecule will be inactive for ESR (taking $:\ddot{O}=Q:$
state). Mo(V) disappears as follows;

or
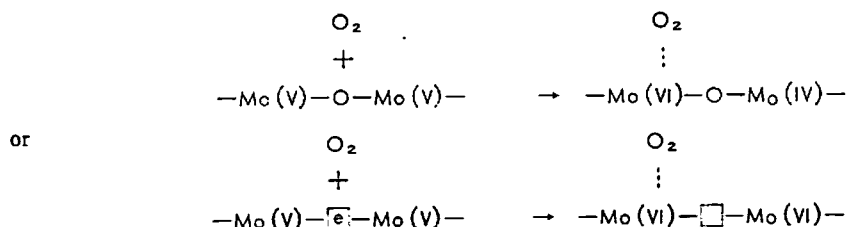
The disappearance of Mo(V) by H_2O adsorption will be also interpreted as in the case of oxygen ad-
sorption.

Acknowledgments

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