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Molybdenum Peroxo Complex. Structure and Thermal Behavior

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The molybdenum peroxide (Mo-y) prepared by oxidation of molybdenum metal with hydrogen peroxide has been studied to determine its structure and thermal behavior. Temperature programmed decomposition has been used to study the thermal stability of Mo-y. Two distinct peaks, I and II, of decomposition processes are discernible in Mo-y. Peak I corresponds to the elimination of water of crystallization and peak II to the decomposition of a peroxide ion of Mo-y. IR and UV examinations support the results of the thermal analysis. The IR band at 931 cm^{-1} and the UV band at 381 nm show the same thermal behavior. Both bands are attributable to the peroxide ion of Mo-y. Spectroscopic studies show that Mo-y has the tetrahedral coordination derived from the single molybdenum complex, which has double bond oxygens attached to Mo atom and has a symmetric type of peroxide ion with one water of crystallization.

Molybdenum peroxide is obtained by oxidation of molybdenum metal powder or molybdenum trioxide with hydrogen peroxide; it has one more oxygen than molybdenum oxide and shows other distinctive features. This molybdenum peroxide (yellow crystallites, abbrreviated as Mo-y) exhibits catalytic activities or acts as an oxygen carrier for a wide variety of organic reactions. For example, Mo-y is active for catalytic dehydration and stoichiometric oxidation of various alcohols and for catalytic epoxidation of various olefinic compounds with *t*-butyl hydroperoxide.[1,2] According to the results derived from these reactions, Mo-y shows dual-function properties: acid properties and oxidation properties as an oxygen carrier.

In the present paper, we describe a neat conclusion about the structure of Mo-y reached by comparing spectral data and thermal behavior.

Experimental

Preparation of Molybdenum Peroxide (Mo-y). The preparation procedure of Mo-y for the work reported here was described in detail previously.[3] In brief, 6.3 g of molybdenum metal powder (Mo: 99.9%, Wako Chemical Co.) was reacted with ice-cooled 50 cm^3 of hydrogen peroxide (30%, Mitsubishi Gas Chemical Co. Ltd.). The solution was maintained below 310 K for 1 h and was allowed to stand for several days at room temperature. A yellow precipitate formed from the solution. The precipitate was collected by filtration and dried under vacuum at room temperature.

Thermal Analysis. Both thermal gravimetrical analysis (TGA) and temperature programmed decomposition (TPDE) experiments were performed under vacuum conditions. About 100 mg of a sample was charged in a quartz basket attached to a standard vacuum system (1×10^{-4} Pa). A McBain type of quartz spiral spring was hung down to the sample basket. The weight change during the TGA experiment was determined by the change in length of the quartz spring (sensitivity: 0.02 mm mg^{-1}), which was equipped with a displacement meter (type 2U, Shinko Electronic Co.).

For TPDE examination, the pressure change of the decomposed gas of the sample was monitored by a vacuum gauge which recorded automatically. Both experiments were operated simultaneously.

Infrared Spectroscopy. A vacuum tight IR cell having KBr windows was designed to fit an infrared spectrometer (260-50, Hitachi Co.) and to be attachable to a vacuum system. Samples (3—5 mg) were dispersed on a thin silicone plate (1×2 cm). The cell was arranged such that a sample plate could be lowered into slots between the optical windows for the spectroscopic examination and withdrawn upward by a magnet into a heated portion (self-contained furnace) for various treatments described below.

UV-Diffuse Reflectance Spectroscopy. A photomultiplexer (R446U, Shimadzu Co.) was attached in the sample cavity of a spectrometer (UV-240, Shimadzu Co.). Each sample of Mo-y (about 50 mg), after a specified heat treatment, was charged into a cell which was covered by a quartz glass plate. $BaSO_4$ was used as a reference.

X-Ray Powder Diffractometry. X-Ray powder diffraction patterns were obtained by a RAD-2A (Rigaku Electronic Co.) diffractometer. The sample of X-ray analysis were the same samples as used for the UV measurements mentioned above.

Results and Discussion

Thermal Analysis. A Mo-y sample which had been previously dried under vacuum at room temperature was evacuated at 323 K for 2 h in the system. A small amount of physically adsorbed water was desorbed during this treatment. TGA and TPDE were carried out from 323 K up to 600 K, and the temperature was raised at various constant rates (4—10 K min^{-1}). Figure 1 shows the TGA curve which was obtained under vacuum conditions. The weight de-

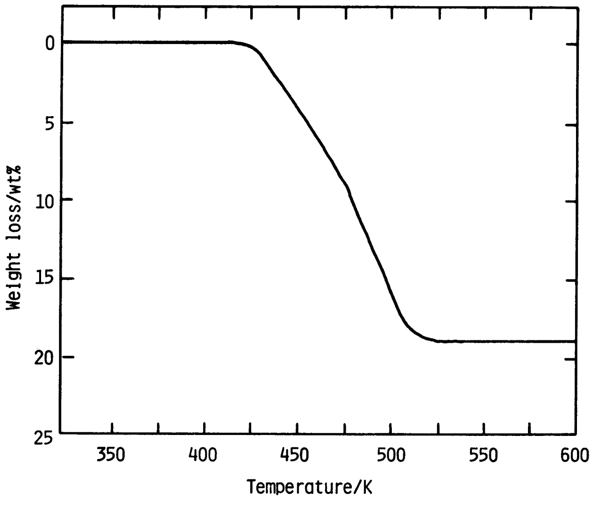


Fig. 1. TGA curve of Mo-y. Heating rate: 5 K min^{-1}.

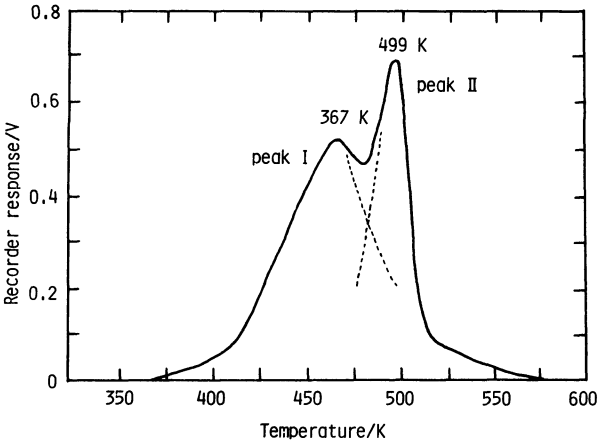


Fig. 2. TPDE spectrum of Mo-y. Heating rate: 5 K min^{-1}.

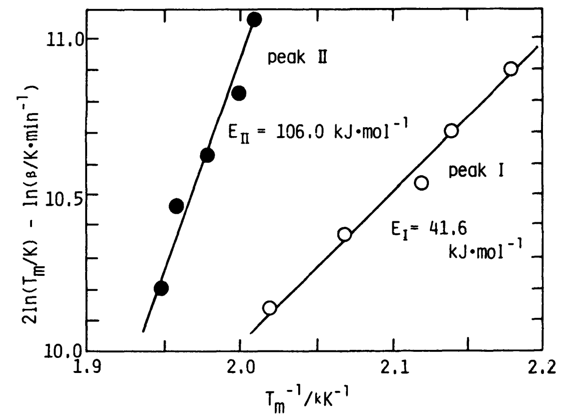


Fig. 3. Arrhenius plots for decomposition of Mo-y. T_m: Temperature of the maximum rate of decomposition for peaks I and II, β: heating rate (K min^{-1}).

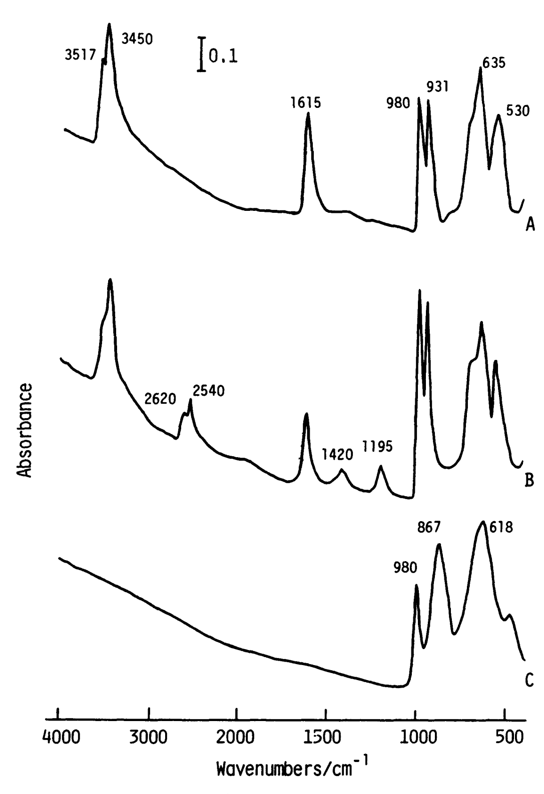


Fig. 4. IR spectra of Mo-y after various treatments. A: Evacuated at room temperature for 2 h, B: exchanged with gaseous D_2O at room temperature, C: evacuated at 673 K.

crease started about 420 K and completed at around 530 K. A well-reproduced weight decrease was observed, based on the weight of the starting Mo-y: it amounted to 19.1±0.1 wt%. The TGA curve represents a one-stage decomposition of Mo-y. However, the curve at around 470 K (10—13 wt% decrease) shows a slight *S* shape.

It is clear that the TPDE spectrum in Fig. 2 represents a two-stage decomposition of Mo-y. When the contributions of these peaks are estimated, the area ratio of peak I at 367 K to peak II at 499 K is about 2 to 1. This result suggests that the thermal decomposition of Mo-y has two kinds of decomposition species. Theoretical derivations[4] give Eq. (1) for the TPDE experiments:

$$\frac{d \ln (T_m^2/\beta)}{d \ln (1/T_m)} = \frac{E_d}{R} \qquad (1)$$

where T_m is the temperature which corresponds to the maximum rate of decomposition for a sample, β is the heating rate, and E_d is the activation energy for the decomposition. Figure 3 shows the Arrhenius plots for the decomposition of Mo-y; these were derived from Eq. (1) at various heating rates (4—10 K min^{-1}). The slopes for peaks I and II in Fig. 3 yield activation energies of 41.6 kJ mol^{-1} and 106.0 kJ mol^{-1}, respectively. A result for peak I shows elimination of some relatively weaker chemical species, which could be related to the water molecules generated from Mo-y. On the other hand, the activation energies for peak II represent the decomposition of Mo-y; this peak has rather higher thermal stabilities than peak I. Thus peak II must be correlated to the decomposition of peroxide ion of Mo-y.

Infrared Spectroscopy. Figure 4 (A) shows the IR spectrum of Mo-y evacuated at room temperature in the vacuum cell. After 1 h, the vacuum conditions inside the cell reached 1×10^{-4} Pa. The OH asymmetrical and symmetrical stretching frequencies were observed at 3517 cm^{-1} and 3450 cm^{-1}, together with OH bending vibration of water molecules at 1615 cm^{-1}, respectivery. It can be seen that water molecules of Mo-y are rather easily replaced by D_2O molecules at room temperature (P_{D_2O}=0.7 kPa). OD stretching bands in spectrum (B) were observed at 2620 cm^{-1} and 2540 cm^{-1}, while the bending modes for HDO and D_2O were also observed at 1420 cm^{-1} and 1195 cm^{-1}. The IR sample was evacuated at various temperatures, which were chosen from the characteristics of the results of TGA and TPDE experiments. The relationship between the normalized integrated intensities of OH stretching and bending bands at various evacuation temperatures gives a straight line going through the origin, as shown in Fig. 5. These results suggest that the water molecule is attached to the molybdenum peroxide molecule with a hydrogen bond. There is no evidence of Mo–OH bonding because the stretching frequencies are relatively lower (3517 and 3450 cm^{-1}) than that of water molecules at 3652 cm^{-1}.[5]

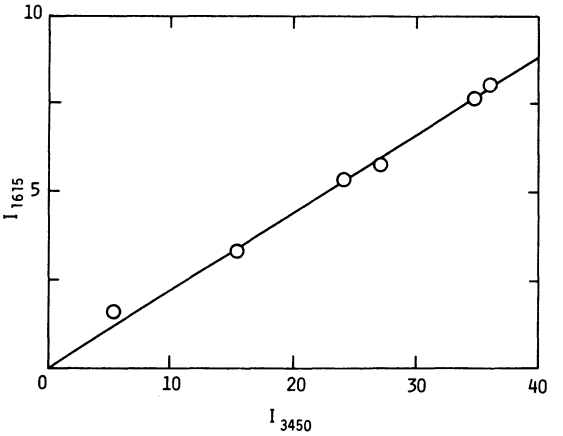


Fig. 5. Integrated intensities of OH stretching and bending vibrations of Mo-y for various evacuation temperatures.

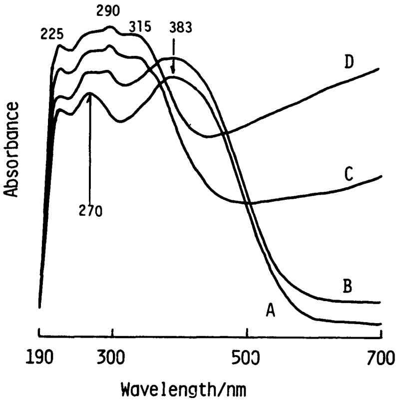


Fig. 6. UV-diffuse reflectance spectra of Mo-y after various treatments. A: Evacuated at room temperature, B: evacuated at 423 K, C: evacuated at 503 K, D: evacuated at 583 K.

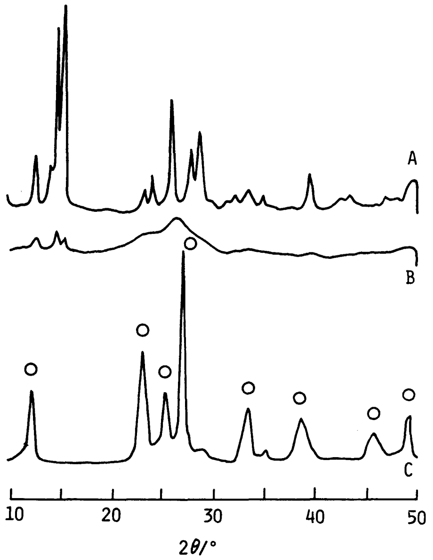


Fig. 7. XRD patterns of Mo-y evacuated at various temperatures. A: Room temperature, B: 473 K, C: 623 K.

At the lattice vibration region of oxides, spectrum (A) shows the stretching vibration of Mo=O,[6] which gives a band at $980\,cm^{-1}$; this band was also observed in spectrum (C), for the sample evacuated at 673 K. Asymmetric and symmetric stretching of Mo–O were observed at $635\,cm^{-1}$ and $530\,cm^{-1}$, respectively. No bands of bridging oxygen for Mo–O–Mo[7] were obserbed in spectrum (A). However, after evacuation at 673 K, spectrum (C) shows the bands of Mo–O–Mo at $867\,cm^{-1}$ and $618\,cm^{-1}$. Furthermore, the band at $931\,cm^{-1}$ in spectrum (A) also disappeared in spectrum (C); this band could be attributed to the O–O stretching vibration of the peroxy structure of Mo-y. In general, the O–O vibration of superoxide ion (O_2^-) and peroxide ion (O_2^{2-}) appears at *ca.* $1140\,cm^{-1}$ and *ca.* $800\,cm^{-1}$, respectively.[8] However, the O–O stretching frequencies of the symmetric type of peoxide ion appear lower between $932\,cm^{-1}$ to $742\,cm^{-1}$;[9] their location seems to depend on the electronegativities of each transition metal. Mimoun *et al.*[10] ascribed the band of vanadium peroxo complex ranging from $940\,cm^{-1}$ to $935\,cm^{-1}$ to the O–O stretching vibration. As was stated previously, the O–O stretching can be observed in a broad region. But the assignment of the O–O stretching of Mo-y is supported by the results of the thermal analysis. According to the TPDE spectrum in Fig. 2, the thermal decomposition corresponding to peak II seems to coincide with the properties of the band at $931\,cm^{-1}$, which can be attributed to the decomposition of the peroxide ion of Mo-y.

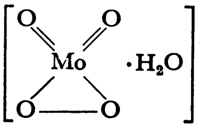
UV-Diffuse Reflectance Spectroscopy. The UV-diffuse reflectance spectra of Mo-y after various treatments are shown in Fig. 6. Spectrum (A) showed a $2t_2$ to $3t_2$ transition at 225 nm and a t_1 to $3t_2$ adsorption at 270 nm; these are associated with the charge transfer bands of a $Mo^{6+}{=}O^{2-}$ for the tetrahedral coordination derived from the single molybdenum complex.[11] The additional band at 383 nm in spectra (A) and (B) disappeared after evacuation at temperatures 505 K to 583 K in spectra (C) and (D). The spectra (C) and (D) are quite similar to the authentic spectrum of molybdenum trioxide. These are not characteristic of the tetrahedral coordination: in comparison with spectrum (A), both (C) and (D) have an additional band (290 nm or 315 nm) which corresponds to the octahedral coordination of Mo^{6+}.[12]

X-Ray Diffractometry. Figure 7 shows the XRD patterns of Mo-y. (A) is freshly prepared Mo-y; this was the same sample as used for the UV examinations. The finely crystallized particles of Mo-y became amorphous after evacuation at 473 K; this pattern is shown in (B). (C) shows the sample after evacuation at 623 K. Almost all the lines obtained here in (C) are superimposed on the lines of authentic crystallites of molybdenum trioxide which is marked as open circle. The results shows the rearrangements of the lattice structure of Mo-y from tetrahedral to another that might be octahedral in configuration.

The results of the TGA and TPDE measurements suggest that the 19.1 wt% weight decrease is equivalent to the loss of one molecule of water of crystallization and half a molecule of oxygen gas from Mo-y, as shown in Eq.(2):

$$[MoO_4\cdot H_2O] \xrightarrow{\Delta} MoO_3 + H_2O + 1/2O_2. \tag{2}$$

The elimination of water of crystallization occurred at a somewhat lower temperature (peak I in Fig. 2) than that of peroxide ion (peak II) of Mo-y. Spectroscopic investigations show that Mo-y consists of the tetrahedral coordination derived from a single molybdenum complex, which has double bond oxygens attached to the Mo atom and has a symmetric type of peroxide ion with one water of crystallization. The idealized structure of Mo-y can be shown as Scheme 1.



Scheme 1.

Vanadium (V) peroxo complexes which homolytically cleave to give V^{4+}-OO· species are different from the known molybdenum or tungsten peroxo complexes which heterolytically cleave to M^{+}-O-O^{-} species.[10] The O-O vibration of Mo-y appears at higher wave number region. This result is similar to that of vanadium peroxo complexes reported by Mimoun *et al.*,[10] and it may be ascribable to Mo-y having a different reactivity from other peroxo complexes which react heterolytically.

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