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Thermal Behavior of a New Type Molybdenum Oxide Obtained by Oxidation of Molybdenum Powder or Molydenum Trioxide with Hydrogen Peroxide

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Synopsis. New molybdenum oxides, Mo-y(yellow) and Mo-b(blue), were obtained by the reaction between molybdenum powder or molybdenum trioxide and hydrogen peroxide. Their reactivity and structure were examined by iodometry, IR, X-ray, and thermal analyses. Mo-y is an acidic oxidant but Mo-b is acidic.

A new type of molybdenum oxide(Mo-y) was obtained by oxidation of molybdenum powder or molybdenum trioxide with 30% hydrogen peroxide. A blue molybdenum compound(Mo-b) was produced by the reaction of molybdenum powder with an inadequate amount of 30% hydrogen peroxide. On the other hand, an excess 30% hydrogen peroxide produced yellow powder(Mo-y). Mo-y and Mo-b have catalytic activity for the dehydration of alcohols, Mo-y being more reactive than Mo-b. Mo-y oxidizes iodide ion, the content of which was determined by iodometry. The result shows that Mo-y has a reactive oxygen. Mo-b does not oxidize iodide ion. In order to investigate the reactivity, the thermal behavior of the active sites of Mo-y was studied. The structural change of Mo-y caused by heating was investigated by means of IR, TG, DTA, and X-ray.

Results and Discussion

Reaction with Hydrogen Peroxide. The reaction scheme is shown in Fig. 1.

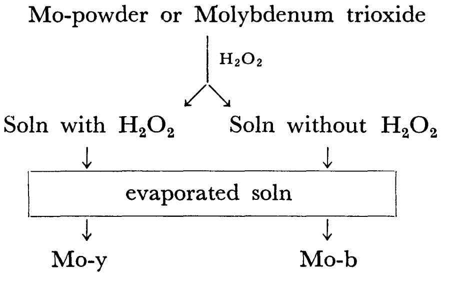

Fig. 1. Reaction path of molybdenum powder or molybdenum trioxide and hydrogen peroxide.

The analysis shows that there is one active oxygen to one atom of molybdenum in Mo-y, indicating the possibility of the existence of a OOH group, while Mo-b has no active oxygen. It seems that Mo-b has OH groups but not a OOH group. Mo-b is synthesized from molybdenum powder but not from molybdenum trioxide. Mo-y, however, is obtained from molybdenum powder or molybdenum trioxide. Glemser and Lutz[1] reported that the structure of molybdenum oxide hydroxide is $MoO_{3-x}(OH)_x$ ($0.5 \leq x \leq 2$). Wilhelmi[2] investigated the MoO_3 and MoO_2 prepared from MoO_3 by reduction with hydrogen at 500 °C and proposed the structure $Mo_4O_{10}(OH)_2$. In this paper, Mo-b is indicated by $MoO_2(OH)_2$ and Mo-y by $MoO_2(OH)(OOH)$.

Differential Thermal Analysis(DTA) and Thermal Gravimetric Analysis(TG). The sample was dried at 30 °C for 72 h under reduced pressure before measurement. DTA and TG curves are shown in Fig. 2. Mo-y showed a gradual decrease in weight up to 200 °C. Above 200 °C, endothermic change takes place with an abrupt decrease in weight, the active oxygen disappearing and Mo-y being transformed into molybdenum trioxide. The weight decrease at 200 °C is calculated from the TG curve to be one mole of water and one gram atom of active oxygen, an endothermic peak was observed and later an exothermic peak, molybdenum trioxide being transformed from amorphous into crystalline form. The weight decrease observed for Mo-b up to 200 °C is calculated to be due to the disappearance of water. The final product was shown to be molybdenum trioxide by IR and X-ray analyses. The DTA curve shows an exothermic peak, the amorphous compound becoming crystalline molybdenum trioxide.

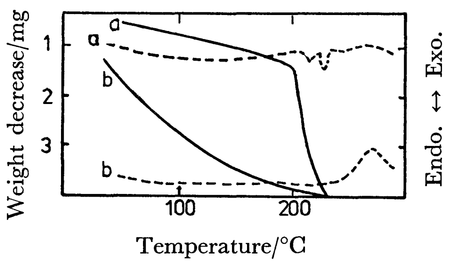

Fig. 2. DTA-TG curves of Mo-y and Mo-b.
a: Mo-y (18.3 mg), b: Mo-b (18.3 mg),
——: TG, ----: DTA, 5 °C/min.

IR Spectrum. For Mo-y, OH stretching frequency and OH deformation vibration were observed at 3450 and 1620 cm^{-1} respectively. The symmetrical terminal Mo–O stretch occurs around 930 cm^{-1} and the antisymmetrical terminal Mo–O stretch at 950 cm^{-1}. The absorption bands are the same as those reported by Mimoun *et al.*[3] and Sotani *et al.*[4] for molybdenum compounds. Absorptions at 980 cm^{-1} are derived from the active oxygen in Mo-y, since the amounts of active oxygen determined by iodometry are associated with the absorbance at 980 cm^{-1} (Fig. 3(A)). The band is assigned to the Mo–O–O stretching vibration. In the case of Mo-b, the region of OH absorption band is the same as that for Mo-y (3400 and 1610 cm^{-1}). The absorption peaks are observed at 970 and 910 cm^{-1}. Probably the band at 930

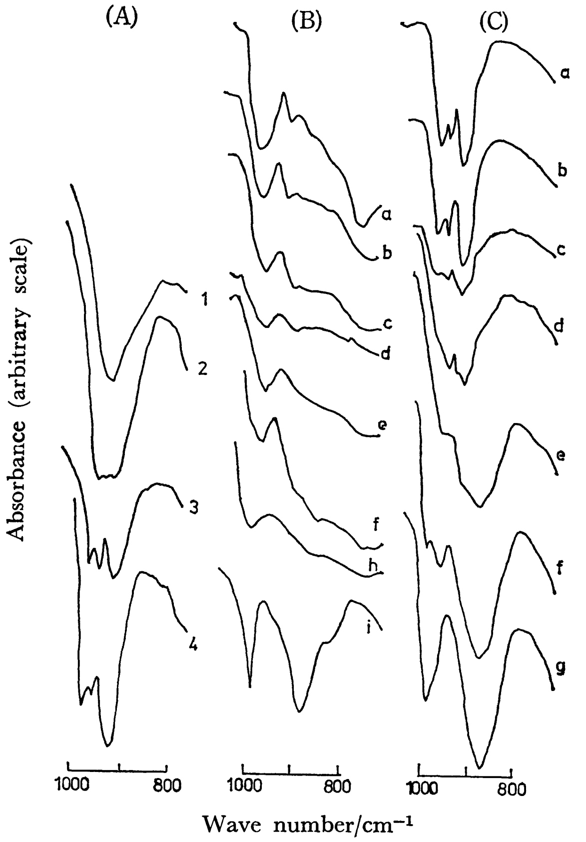

Fig. 3. IR spectra and amount of active oxygen of the molybdenum compound oxidized with hydrogen peroxide (A). Amount of active oxygen (mmol/g); 1: 0.11, 2: 0.13, 3: 3.23, 4: 4.04.
IR spectra of Mo-b(B) and Mo-y(C) at various temperatures of calcination.
a: 30 °C, b: 100 °C, c: 130 °C, d: 160 °C, e: 185 °C, f: 200 °C, g: 220 °C, h: 240 °C, i: 260 °C.

cm^{-1} shifted to the lower wave number region (910 cm^{-1}) owing to the hydrogen bond from absorbed water and the Mo–O bond. The absorption band of the deformation vibration (rocking) mode of the water molecule coordinated with metal was observed at 750 cm^{-1}. Mo-y and Mo-b were dried under reduced pressure in an oven at 30 °C for 72 h. Mo-y treated in the manner described above was calcined under reduced pressure for 1 h at 100, 130, 160, 185, 200, and 220 °C, and Mo-b at 100, 130, 160, 185, 200, 240, and 260 °C. The IR spectra were observed with a KBr tablet. Figure 3(B), (C) show the change of range 1000—800 cm^{-1}. Both compounds turn into molybdenum trioxide above 200—240 °C. The absorption bands of Mo-y at 980, 950 and 930 cm^{-1} assigned to Mo–O gradually decrease by heating up to 200 °C, followed by the disappearance of active oxygen and the appearance of the absorbance of molybdenum trioxide. Upon heating Mo-y, a band was observed at 920 cm^{-1}. It can be assumed that the band at Mo–O shifts to lower wave numbers owing to the increase of polarization of the Mo–O bond. In the case of Mo-b, the Mo–O stretching frequency at 970 cm^{-1} shifts to 990 cm^{-1}. The absorption band at 910 cm^{-1} arising from the Mo–O bond, shifts to 870 cm^{-1}, the band being characteristic of the Mo–O–Mo bond.

X-Ray Analysis. Krebs$^{5)}$ and Sotani$^{6)}$ reported on the X-ray analysis of molybdenum oxide, but no report seems to have appeared on the X-ray diffraction analysis of molybdenum oxidized with hydrogen peroxide. The measurement was carried out by the powder method. Mo-b is amorphous, a weak broad diffraction band being observed at 0.307—0.263 nm spacing(d). Mo-y has a high crystallinity and the diffractive band of the spacing at 0.169 nm is very strong. It shows a sheet type structure with 0.619 nm spacing. Molybdenum oxide and molybdenum have 0.53 and 0.567 nm spacing, respectively.$^{5,6)}$ This difference might arise from the active oxygen in view of the insertion of oxygen between the sheet type structure.

Experimental

Materials. Molybdenum powder (Tokyo Tangusten K.K. Toyama factory: purity 99.985%, diam. 4.2 μm) and hydrogen peroxide (guaranteed reagent 30% Mitsubishi Gas Chemical Co., Ltd.) were used. All other chemicals (Wako Chemicals Co.) were of first grade.

Analysis. Thermal analysis was carried out with a differential thermal gravimetric microbalance (Rigaku TG-DTA), a heating rate of 5 °C/min and static air atmosphere being employed with 18 mg samples in each run. The infrared spectra were obtained with a Hitachi Infrared Spectrophotometer Model 125 on a KBr disk. X-Ray powder patterns were obtained with nickel filtered Cu *K* radiation. Active oxygen was determined by iodometry. EDTA titration$^{7)}$ was used to measure the content of molybdenum.

Synthesis of Mo-y and Mo-b. Molybdenum powder was added to 30% hydrogen peroxide at 60 °C, a yellow solution being obtained. When the solution became yellow, addition of molybdenum powder was stopped; hydrogen peroxide was then added in order to oxidize the Mo-y satisfactorily. After filtration of unreacted molybdenum powder, the solution was evaporated to give Mo-y as a yellow powder$^{8)}$. When molybdenum powder was added to the yellow solution, the color of the solution turned blue. The blue solution was filtered to remove unreacted molybdenum powder, a blue powder being obtained on evaporation of the solution.

This article is gratefully dedicated to Professor Georg Manecke on the occasion of his sixty-fifth birthday.

References

1) O. Glemser and G. Lutz, *Z. Anorg. Chem.*, **264**, 17 (1951).
2) K. A. Wilhelmi, *Acta Chem. Scand.*, **23**, 419 (1969).
3) H. Mimoun, I. S. de Roch, and L. Sajus, *Bull. Soc. Chim. Fr.*, **1969**, 1481.
4) N. Sotani, Y. Saito, M. Taneda, and M. Hasegawa, *Nippon Kagaku Kaishi*, **1974**, 673.
5) B. Krebs, *Acta Crystallogr., Sect. B*, **28**, 2222 (1972).
6) N. Sotani, *Bull. Chem. Soc. Jpn.*, **48**, 1820 (1975).
7) H. Yaguchi and T. Kajihara, *Bunseki Kagaku*, **14**, 785 (1965).
8) Y. Kurusu and N. Ishii, Japan Patent 52-46793 (1977).