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# Formation of a Hydrogen Insertion Compound of Hydrated Molybdenum Oxide from Hydrogen Molybdenum Bronze

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**Synopsis.** It was found that hydrogen molybdenum bronze, $H_{0.3}MoO_3$, turns into a hydrogen insertion compound of hydrated molybdenum oxide in a 1M HCl aqueous solution at 353 K. It was predictable that the compound has a composition of $H_{0.15}MoO_3 \cdot 0.88H_2O$ and is identical with $Mo_8O_{15}(OH)_{16}$ or a similar compound.

Hydrogen molybdenum bronzes are interesting materials and have been studied extensively.[1-6] The authors have studied the stability of bronzes and have found that one member, $H_{0.3}MoO_3$, changes into a new compound upon treatment at 353 K in a 1M HCl aqueous solution (1 M=1 mol dm$^{-3}$). In the present study, a characterization of this compound was achieved.

## Experimental

**Preparation.** The sample was prepared from $H_{0.3}MoO_3$ in a 1M HCl aqueous solution at 353 K for one week. It was filtrated, washed by water, and then vacuum dried.

**Measurements.** Powder X-ray diffraction patterns were obtained by using a RIGAKUDENKI GEIGER D-1 FLEX diffractometer with Cu *Kα* radiation. Samples for X-ray diffraction measurements were mixed with an internal standard (ca. 5 wt% Si powder). The IR spectra were recorded at room temperature by using a JASCO 701G spectrophotometer. Samples for this measurement were pressed into disks (ca. 0.5 wt% in KBr). TG-DTA was carried out on a MAC SCIENCE TG-DTA 2000 at a heating rate of 10 K min$^{-1}$. The sample weight for the measurement was ca. 20 mg. The hydrogen contents of the samples were determined chemically by Choain and Marion's method.[7]

## Results and Discussion

The prepared sample was powder with a bluish gray color. The X-ray diffraction pattern and IR spectrum of the sample are shown in Figs. 1 and 2, respectively. The observed diffraction peaks in Fig. 1 and the IR bands in Fig. 2 are clearly different from those of $H_{0.3}MoO_3$. Those marked with the symbol ★ in these Figures correspond to those of $MoO_3$. The diffraction peaks with the symbol ○ correspond to those of $Mo_8O_{15}(OH)_{16}$, which have been synthesized from a mixture of $MoO_3 \cdot 2H_2O$ and Mo metal by Glemser and Lutz.[8] According to chemical analysis, the sample contained 0.10 hydrogen atom/Mo atom. Figure 3 shows a TG-DTA curve of the sample. Endothermic peaks appear at 429 and 477 K, and an exothermic peak appears at 621 K. Both endothermic peaks are followed by a large weight loss, which corresponds to 4.2 and 2.6 wt%, respectively. The peak temperature of 429 K is comparable to the releasing temperature of hydrate-water in yellow $MoO_3 \cdot H_2O$.[9] By H-NMR a Pake-doublet ($r$=0.15 nm) can be observed. Thus, the peaks can be attributed to the release of two kinds of hydrate-water, and a gradual weight loss continues until 573 K after their release. The exothermic peak at 621 K is followed by a weight gain (0.2 wt%). The peak might be attributed to the oxidation of the sample. The structural change at each DTA peak has been investigated. The results by X-ray diffraction and IR spectroscopy measurements are also shown in Figs. 1 and 2. With the release of two kinds of hydrate-water, the diffraction peaks and IR bands without the symbol ★ exhibit apparent changes. On the other hand, those with the symbol exhibit no or little change below 573 K. After the exothermic peak, the sample perfectly changes into $MoO_3$. The hydrogen contents of the samples heated at 448, 493, 573, and 673 K were 0.09, 0.07, 0.04, and 0.00 H atom/Mo atom, respectively. This shows that a large portion of the inserted hydrogen atoms are released in the temperature region which corresponds to a gradual TG loss. Thus, the release of hydrogen may be associated with a gradual TG loss. On the basis of the above results, the authors propose that the newly found compound by an HCl treatment of $H_{0.3}MoO_3$ is a hydrogen insertion compound of

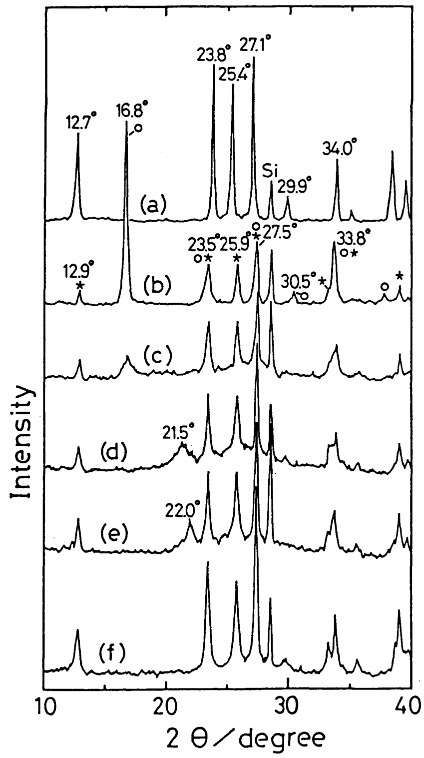

Fig. 1. Powder X-ray diffraction patterns of $H_{0.3}MoO_3$ (a), the sample as prepared (b), the sample heated in air at 448 K (c), at 493 K (d), at 573 K (e), and at 673 K (f).

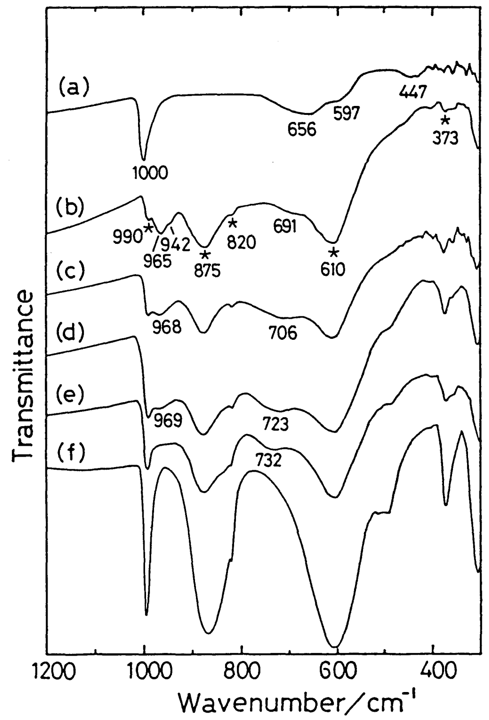

Fig. 2. IR spectra of $H_{0.3}MoO_3$ (a), the sample as prepared (b), the sample heated in air at 448 K (c), at 493 K (d), at 573 K (e), and at 673 K (f).

hydrated molybdenum oxide. However, it is also concluded that the sample is not single phase and contains $MoO_3$.

The total composition of the as-prepared sample was $H_{0.10}MoO_3(H_2O)_{0.59}$. This composition corresponds to a formula of $0.36MoO_3+H_{0.15}MoO_3\cdot 0.88H_2O$ ($0.36MoO_3+0.08Mo_8O_{15.40}(OH)_{15.95}$). This formula means that the content of $MoO_3$ is 33.5 wt%. On the other hand, the content of $MoO_3$, by an estimation from the change in the intensity ratio of the characteristic diffraction peak at 25.9° by adding known amounts of commercial $MoO_3$ to the sample, has been 50 wt%, although the intensity of the peak at 25.9° for $MoO_3$ is appreciably small than that of the peak at 16.8° for the new compound. The real content might deviate from the estimated value to some extent because of the uncertainty of the assumption regarding the estimation that $MoO_3$ in the sample had the same diffraction peak intensity as the commercial one. It is therefore considered that the estimated value supports the above-mentioned large content of $MoO_3$ (33.5 wt%). On the basis of this discussion and the similarity in the X-ray diffraction pattern, the compound can be predicted to be $H_{0.15}MoO_3\cdot 0.88H_2O$ which is identical with $Mo_8O_{15}(OH)_{16}$ or a similar compound. A synthesis of the compound as a single phase is in progress.

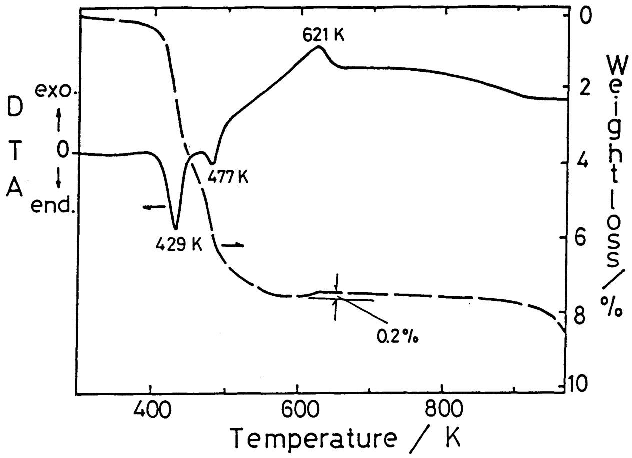

Fig. 3. TG-DTA curve of the sample as prepared.

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