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Infrared Study of Structural and Compositional Changes in Orthorhombic Hydrogen Molybdenum Bronze, $H_{0.3}MoO_3$, by Heating in Vacuo

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Synopsis. Hydrogen molybdenum bronze, $H_{0.3}MoO_3$, heated in vacuo was studied by FT-IR spectroscopy. The spectrum near 1000 cm^{-1} analyzed by a microcomputer system was confirmed to be composed of three bands. Among them, bands at 1005 and 990 cm^{-1} correspond to the Mo=O bonds of orthorhombic bronze and rhombic MoO_3, respectively.

It is well-known that by insertion of atomic hydrogen into MoO_3, the rhombic MoO_3 structure turns to the orthorhombic bronze structure.[1] This structural change is expected to effect strongly on the Mo=O stretching vibration. It is confirmed by thermogravimetry[2] and TPD method[3] that orthorhombic hydrogen molybdenum bronze, $H_{0.3}MoO_3$, is decomposed into $MoO_{2.86}$, a nonstoichiometric compound with the rhombic MoO_3 structure, by heating in vacuo with evolution of H_2O. The change in IR spectra has also been studied on samples heated in vacuo, but no quantitative analysis has been made for the bands in the region 1000—800 cm^{-1} which can be assigned to the Mo=O or Mo–O stretching vibration in molybdenum oxide.[4,5] Because of low infrared transmittance of the samples, IR spectra obtained by a conventional grating IR spectrophotometer were not able to be analyzed quantitatively. In the present work, the authors have studied the dehydrogenation process of hydrogen molybdenum bronzes by using a Fourier transform infrared spectrophotometer directly connected with a microcomputer systems and analyzed in detail how dehydrogenation influenced on changes in the structure and composition. This paper mainly deals with the behavior of the bands near 1000 cm^{-1} assigned to the Mo=O stretching vibration of the samples heated in vacuo.

Experimental

The preparation and identification of orthorhombic hydrogen molybdenum bronze, $H_{0.3}MoO_3$, were described previously.[2,3,6] Samples having various hydrogen contents (formulated as H_xMoO_y) were prepared by heating the bronze at various temperatures in vacuo and in air. The composition was determined by thermogravimetry[2] and by Choain and Marion's method.[7] The samples after heating were pressed into disks (ca. 0.5 wt% in KBr). All spectra were recorded in dry air by a Fourier transform infrared spectrophotometer (SHIMADZU, FTIR-4000: with 2 cm^{-1} resolution) directly connected with the microcomputer system (NEC, PC-9801 F2).

Results and Discussion

The hydrogen molybdenum bronze, $H_{0.3}MoO_3$, with the orthorhombic structure was decomposed to a nonstoichiometric compound with the rhombic MoO_3 structure as follows;[6]

$$H_{0.30}MoO_3 \rightarrow H_{0.21}MoO_{2.95} \rightarrow H_{0.06}MoO_{2.88} \rightarrow MoO_{2.85}.$$

This was confirmed to the dehydration process by mass spectrometry. Atomic hydrogens in samples reacted with lattice oxygens and the water was liberated. At the same time, vacancies were produced.

Figure 1 shows the FT-IR spectra of the samples heated in vacuo. The bands at 999, 650, 590, and 430 cm^{-1} of orthorhombic bronze, $H_{0.30}MoO_3$, are almost the same as those reported by Schroder and Weizel.[8] The intensities of the bands at 999, 650, and 430 cm^{-1} gradually reduced with the decrease in hydrogen content of the samples. On the other hand, new bands appeared in the region 900—800 cm^{-1} and the band at 590 cm^{-1} was intensified as dehydration process proceeded. Figure 1 also shows that the band at 999 cm^{-1} was split into two bands at 1004 and 990 cm^{-1} in the case of the samples with lower hydrogen contents than the lowest limit (x=0.21) of

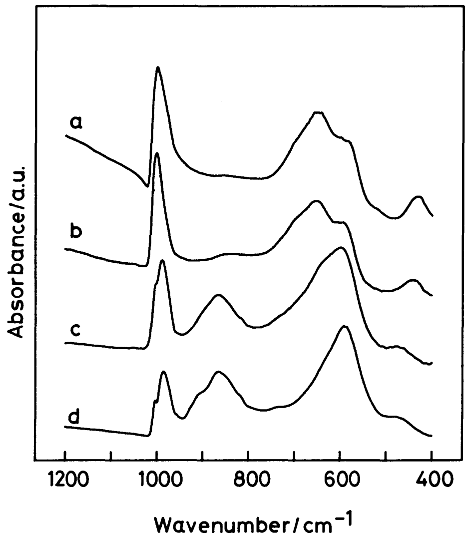

Fig. 1. FT-IR spectra of the samples, H_xMoO_y. a, $H_{0.30}MoO_3$; b, $H_{0.21}MoO_{2.95}$; c, $H_{0.080}MoO_{2.89}$; d, $MoO_{2.85}$.

the orthorhombic structure. This behavior could not be observed clearly by using the grating IR spectrophotometer. It is well-known that the bands near 1000 cm^{-1} can be assigned to the Mo=O stretching vibration in molybdenum oxide.[4,5] The results suggest that samples with lower hydrogen contents than x=0.21 give at least two kinds of the Mo=O stretching vibration. While in the case of the bronze heated in air, only the bands due to MoO_3 appeared at 993, 878, and 820 cm^{-1}, though a small amount of hydrogen remained. By thermogravimetry and mass spectrometry, atomic hydrogens inserted in the sample were removed easily as hydrogen molecules in this case. The samples gave immediately the rhombic MoO_3 structure. Therefore, the bands also appeared at the same frequencies with those of MoO_3.

In the previous work,[6] the authors observed the band at 1004 cm^{-1} due to the Mo=O stretching vibration of the orthorhombic bronze and the one at 998 cm^{-1} for the rhombic MoO_3. This suggests that the band shifts of Mo=O stretching vibration was caused by a structural change. As shown in Fig. 1, the band near 1000 cm^{-1} was at least composed of two peaks. Therefore, the band shape analysis has been carried out to obtain further information of the Mo=O bonds by a microcomputer system using the same techniques described previously.[9,10] Although there exists no theoretical justification for IR bands of solid to fit any specific functional form, the Gaussian form was applied.[9] One of the results in the region 1050—950 cm^{-1} is shown in Fig. 2. The band was confirmed to be overlapped by three bands with peaks at 1005, 990, and 972 cm^{-1}, although the original band has two peak maxima. The convoluted curve of these separated bands fits in well with the original spectrum. Thus all spectra of the samples gave three bands with the peaks at nearly the same frequencies in the region 1050—950 cm^{-1}. These results led to the conclusion that the band near 1000 cm^{-1} of each sample is composed of three kinds of Mo=O stretching vibration which shows the peaks at 1005, 990, and 972 cm^{-1}, respectively.

The intensity of each band calculated for unit weight of the samples in disks is plotted against the hydrogen content of the sample as shown in Fig. 3. From this result the intensity ratio of each band to the sum of three bands is calculated at the same hydrogen content as shown in Fig. 4. The value of 1005 cm^{-1} band decreases monotonously, while that of 990 cm^{-1} increases, as hydrogen content decreases. The intensity ratio of the band at 1005 cm^{-1} to that of the

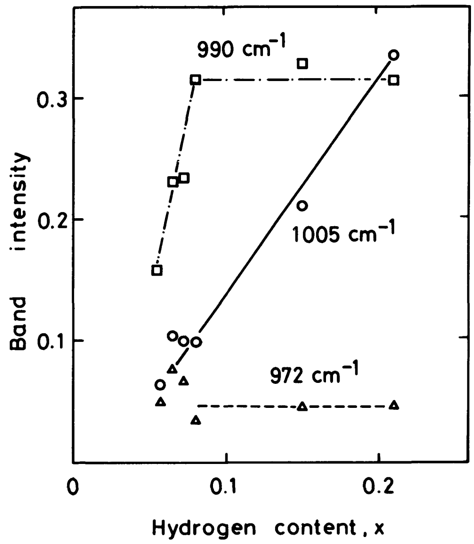

Fig. 3. Relationship between intensity of each band and hydrogen content, x, of the samples; 1005 cm^{-1} (○), 990 cm^{-1} (□), 972 cm^{-1} (△).

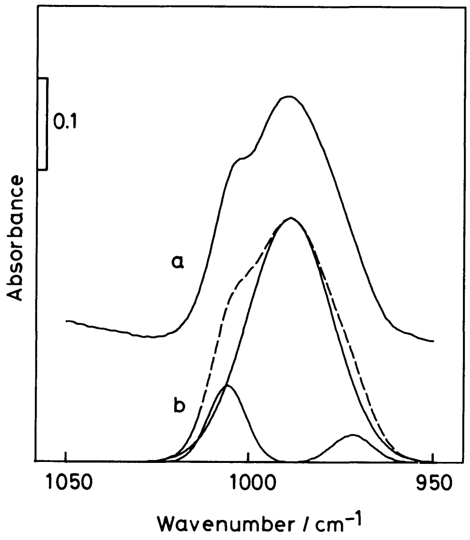

Fig. 2. An example of band shape analysis in the region 1050—950 cm^{-1} (sample: $H_{0.080}MoO_{2.89}$). a, original spectrum; b, separating peaks (——) and convoluted curve (----).

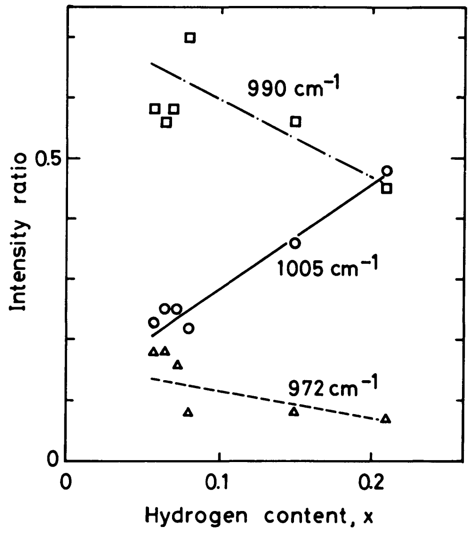

Fig. 4. Relationship between intensity ratio of each band to the sum of three bands and hydrogen content, x, of the samples; 1005 cm^{-1} (○), 990 cm^{-1} (□), 972 cm^{-1} (△).

band at 990 cm^{-1} is calculated from the values in Fig. 4. The ratio is 0.48/0.45=0.52/0.48 at x=0.21, 0.36/0.56=0.39/0.61 at x=0.15, and 0.22/0.70=0.24/0.76 at x=0.08, respectively. These values are in close agreement with the ratios of the orthorhombic to rhombic components obtained from the X-ray and thermogravimetric data.[6] Thus, it is concluded that the band at 1005 cm^{-1} is assigned to the Mo=O stretching vibration of the orthorhombic bronze formed by the insertion of hydrogen atom and that at 990 cm^{-1} is assigned to that of the oxide with rhombic MoO_3 structure. It is clear that existence of the atomic hydrogen induced the change of crystal structure which is strongly correlated with the mode of Mo=O bond as described previously (see Fig. 3 in Ref. 6). On the other hand, the ratio of band at 972 cm^{-1} is small in the whole region and gradually increased as the hydrogen content decreased. It is not sure that this band can be assigned to another kind of Mo=O stretching vibration of polymolybdate such as Mo_4O_{11}, Mo_9O_{26}, and so forth.

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