Bull. Chem. Soc. Jpn., 62, 903—907 (1989)

Preparation and Characterization of Hydrogen Molybdenum Bronzes, H_xMoO_3

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(Received September 9, 1988)

Hydrogen molybdenum bronzes, H_xMoO_3, of Type-I (x=0.21), Type-III (x=1.55), and Type-IV (x=1.90) were prepared by the Glemser's method. Type-II (x=0.91) was obtained from Type-III by standing in air for 120 days. The bronzes with low hydrogen contents were stable, but those with high contents were not so stable. All these bronzes have been studied by X-ray diffraction, IR spectroscopy, and TG-DTA. Bronzes with high hydrogen contents were changed upon heating in air, successively, to those with low hydrogen contents by the evolution of H_2.

Hydrogen molybdenum bronzes, H_xMoO_3 ($0<x\leqq2$), are obtained from MoO_3 by reduction in an acidic media[1,2] and hydrogen spillover.[3] Recently, Birtill and Dickens[4] have confirmed four distinct phases in the range $0<x\leqq2$ and their ranges of homogeneity with the approximate limit: Type-I (blue, orthorhombic), $0.23<x<0.4$; Type-II (blue, monoclinic), $0.85<x<1.04$; Type-III (red, monoclinic), $1.55<x<1.72$ and Type-IV (green, monoclinic), $x=2$. Among these phases, Type-I has been characterized by many authors using X-ray diffraction,[4] neutron diffraction,[5] thermal decomposition,[6-8] IR,[9-11] and NMR.[12,13] The catalytic activity for 1-butene isomerization on Type-I was also studied and the effect of hydrogen atoms on catalytic activity has been confirmed.[9] On the other hand, there are several reports on Type-III studied by NMR.[12-14] Its catalytic activity for hydrogenation reaction has been reported.[15,16] However, Type-II and Type-IV have not been characterized completely because of instability.

The authors have studied[6-8] precisely the thermal decomposition of Type-I by vacuum heating and have discussed its decomposition mechanism. We also attempted to study other phases of bronzes. However, it was very difficult to prepare all types of bronze and to isolate them. The purpose of this work was to prepare all phases of hydrogen molybdenum bronzes and to characterize them by X-ray diffraction, IR spectroscopy, and TG-DTA.

Experimental

Preparation of Hydrogen Molybdenum Bronzes. All phases of hydrogen bronzes were obtained by the Glemser's method.[1]

Type-I. 30 g of MoO_3 was suspended in a 2—3 M (mol l^{-1}) HCl aqueous solution at 0—10 °C. 5 g of Zn powder was divided into several portions; about 1 g of Zn powder was introduced every after nascent hydrogen was stopped to generate. When all the Zn powder was consumed the sample was filtrated, and washed with 2—3 M HCl and then water. The sample was blue and the X-ray result was identical with that of Birtill and Dickens.[4] The hydrogen content was determined to be x=0.21 by chemical analysis.[17] Type-I was very stable, even after standing in air for more than six months.

Type-II. It was very difficult to isolate only one phase of Type-II by the Glemser's method.[1] Type-II was obtained from Type-III by standing in air for at least 120 days. The color was blue and the X-ray result was identical to that of Birtill and Dickens.[4] The hydrogen content was x=0.91. This was stable for more than two months.

Type-III. Type-III was prepared from MoO_3 or Type-I by repeating from three to five runs of the same method described above. The color was red and the X-ray result was identical to that of Birtill and Dickens.[4] The hydrogen content was x=1.55. This was stable for about 10 days (Fig. 1). According to X-ray results, Type-II appeared after Type-III had stood in air for at least 11 days; it increased gradually. Type-III was completely transformed to Type-II by 120 days.

Type-IV. Type-IV was prepared from Type-III by repeating one to two runs of the same method. The sample

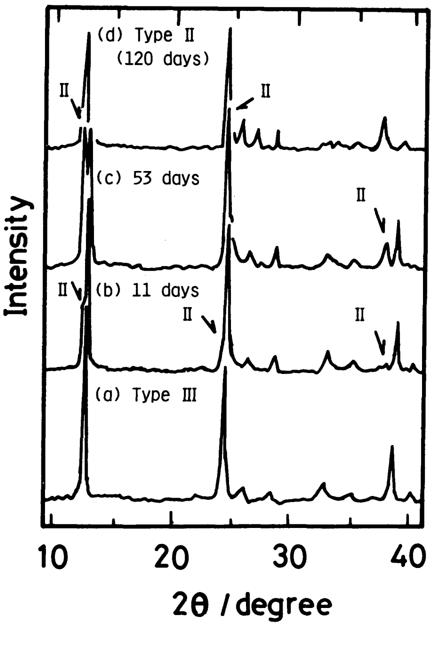

Fig. 1. Changes of X-ray diffraction patterns of Type III by standing in air. (a): Type III (immediately after filtration), (b): stood for 11 days, (c): stood for 53 days, and (d): Type II (stood for 120 days).

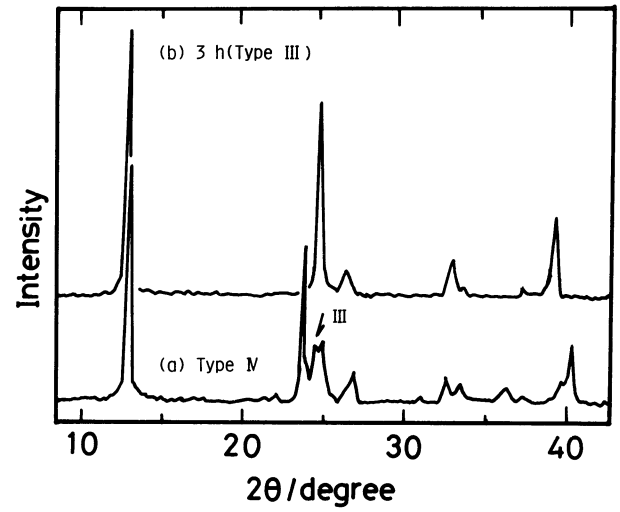

Fig. 2. Changes of X-ray diffraction patterns of Type IV by standing in air. (a): Type IV (immediately after filtration) and (b): stood for 3 h (Type III).

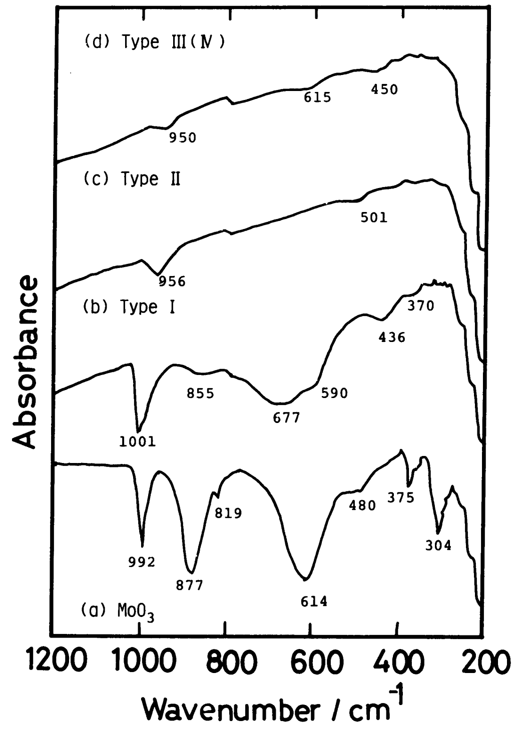

Fig. 3. IR spectra of hydrogen molybdenum bronzes.

began to decompose immediately after being washed with water and completely transformed to Type-III within three hours (Fig. 2).* However, it kept the Type-IV phase when it was filtrated by a suction filter without washing. Type-IV was green in color and the X-ray result was identical to that of Birtill and Dickens.[4] The hydrogen content was x=1.90. When this sample was left standing in a 2—3 M HCl aqueous solution it kept its monoclinic structure and green color for about seven days.

Characterization of Hydrogen Molybdenum Bronzes. Samples were observed and identified by a powder X-ray diffraction method. IR spectra were obtained by using JASCO 701G and SIMADZU FTIR-4000 spectrophotometers. TG-DTA curves were carried out on a MAC SCIENCE TG-DTA 2000 with a heating rate of 10 K min^{-1}. The hydrogen contents of hydrogen bronzes were determined chemically by the Choain and Marion's method.[17]

Results and Discussion

Figure 3 shows the IR absorption bands at 1001, 855, 677, 590, 436, and 370 cm^{-1} for Type-I, at 956 and 501 cm^{-1} for Type-II, and at 950, 615, and 450 cm^{-1} for Type-III. The spectrum of Type-IV is nearly the same to that of Type-III. MoO_3 shows bands at 992, 877, 819, 614, 375, and 304 cm^{-1}. By the insertion of hydrogen atoms into the MoO_3 layers, the band at 992 cm^{-1} in MoO_3 shifted to 1001 cm^{-1} in Type-I. The bands at 877 and 819 cm^{-1} decreased in intensity. A small band at 855 cm^{-1} in Type-I with x=0.21 remained, but Type-I with x=0.34 showed no detectable band in this region. The band in this region appeared and gradually increased,[10,11] when Type-I was heated in vacuo. This suggests that the band at 855 cm^{-1} may have been due to a residual MoO_3 framework which is not completely reduced to Type-I. This leads to the conclusion that the insertion of hydrogen atoms causes a rearrangement of octahedron from the MoO_3 structure to the structure of Type-I (Fig. 4). Berrclough et al.[19] have assigned the band at 992 cm^{-1} to Mo=O(1), that at 877 cm^{-1} to Mo–O(3,3′)–Mo, and that at 819 cm^{-1} to Mo–$\underset{\substack{|\\ \mathrm{Mo}}}{\mathrm{O}}$(2′)–Mo in MoO_3. On the other hand, Py and Maschke[20] have interpreted the experimental results of MoO_3 by using a modification of the intralayer force constants proposed by Beattie et al.[21] According to their calculation,[20] bands at 877 and 819 cm^{-1} in MoO_3 can be assigned to Mo–O(3,3′)–Mo and the band at 614 cm^{-1}, to Mo–$\underset{\substack{|\\ \mathrm{Mo}}}{\mathrm{O}}$(2′)–Mo.

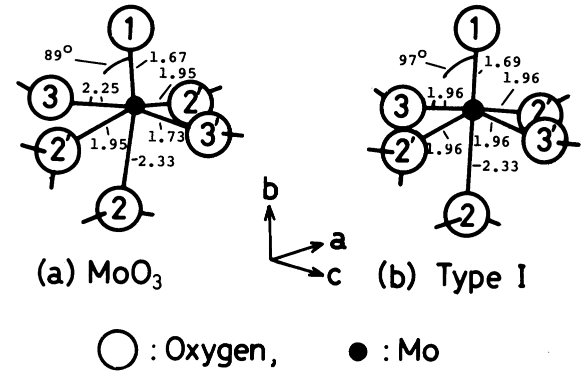

Fig. 4. Schematic model of coordination of oxygen atoms around the molybdenum atom. Unit of numerals is Å.

According to Kihlborg,[18] a schematic model of the oxygen atoms around a molybdenum atom is shown in Fig. 4. The bond length in MoO_3 of Mo–O(2′), Mo–O(3), and Mo–O(3′) is 1.95, 2.25, and 1.73 Å, respectively. By insertion of atomic hydrogen into MoO_3, the bond length of Mo–O(3) is shortened to 1.96 Å and that of Mo–O(3′) is lengthened to 1.96 Å. The bond length of Mo–O(2′) and Mo–O(3,3′) become equal in Type-I. The bond length of Mo=O(1) is lengthened from 1.67 Å in MoO_3 to 1.69 Å in Type-I. The bond angle of O(1)–Mo–O(3) changes from 87° in MoO_3 to 97° in Type-I.

It has been reported[9,12,13] that a hydrogen atom connects with terminal oxygen (Mo=O(1)). This suggests that the bond strength of a doubly bonded terminal Mo=O(1) may be weakened; this may cause a shift to lower frequencies. In fact, a shift from 998 to 1001 cm^{-1} takes place. This result is not understandable in terms of the bond strength; other effects should possibly be considered. No large change in the bond length has been observed between MoO_3 and Type-I, while the bond angle of O(1)–Mo–O(3) changes upon the insertion of hydrogen atoms as mentioned above. The change of this bond angle may effect the stretching vibration of Mo=O(1). According to Py and Maschke,[20] the band at 614 cm^{-1} in MoO_3 has been assigned to Mo–O(2′)–Mo with a bond length of 1.95 Å. The bond length of Mo–O(2′,3,3′) in Type-I is 1.96 Å; this is very similar to that of Mo–O(2′)–Mo in MoO_3. Therefore, the band at 677 cm^{-1} in Type-I should be due to Mo–O(2′,3,3′)–Mo.

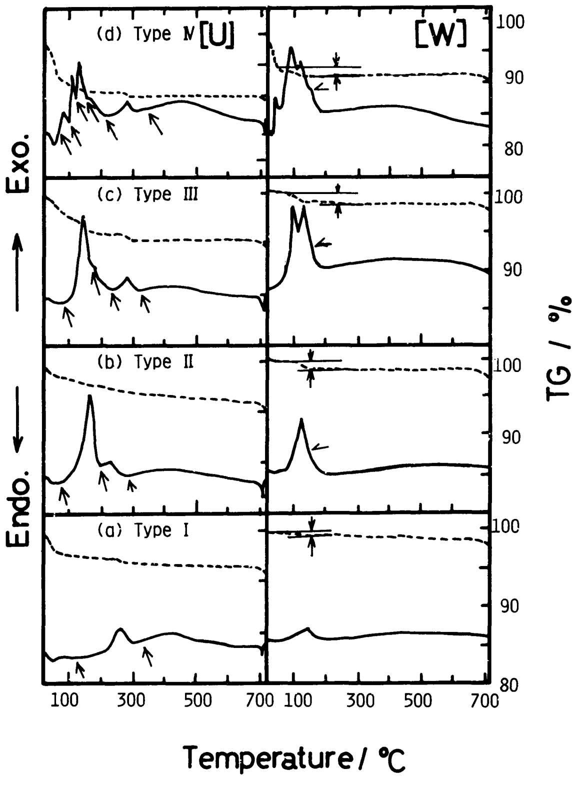

Fig. 5. TG-DTA curves of hydrogen molybdenum bronzes.
—: DTA, -----: TG; [U]: unwashed, and [W]: washed with water.

In the range of Mo–O stretching vibration, Type-II and Type-III(IV) show bands at 956 and 950 cm^{-1}, respectively. The band at 1001 cm^{-1} in Type-I shifts to lower frequencies. This is reasonable because Type-II and Type-III(IV) contain more hydrogen atoms than Type-I; a difference in the structure exists between Type-I (orthorhombic) and Type-II, Type-III, and Type-IV (monoclinic). These hydrogen atoms also attach to terminal oxygen and the bond strength of Mo=O(1) is weakened. The authors are studying by NMR the bahavior of hydrogen atoms in all phases. Considering the NMR results, a precise assignment of the band in Type-II and Type-III(IV) will be reported elsewhere.

Figure 5 shows TG-DTA curves of hydrogen molybdenum bronzes. [U] indicates an unwashed sample which was filtrated and immediately sucked dry. [W] indicates a sample washed with 2—3 M HCl, then washed with water and sucked dry. [U] of Type-I shows an exothermic peak at 263.6 °C and an endothermic peak at 709.4 °C. While [W] of Type-I shows the exothermic peak at 148.6 °C. The exothermic peak of [W] is lower than that of [U]. Each

Table 1. Peak Temperature of DTA Curves and Composition of Bronze at Each Stage

Type	Peak temperature/°C		
	[U]	[W]	Composition
I	709.4		
			MoO_3
	263.6	148.6	
			Type I
II	712.1		
			MoO_3
	221.5	156.6	
			Type I
	158.5	130.0	
			Type II
III	712.8		
			MoO_3
	279.4	151.1	
			Type I
	159.5	131.4	
			Type II
	136.8	99.3	
			Type III
IV	712.2		
			MoO_3
	275.2 (152.1)	151.9	
			Type I
	126.7	123.0	
			Type II
	100.4	91.0	
			Type III
	75.7	47.2	
			Type IV

[U] of all phases of hydrogen bronzes show an endothermic peak at near 710 °C; [W] does not. Exothermic peaks of all phases of [U] arise at higher temperature than those of [W]. All peak temperatures are shown in Table 1. DTA curves of [U] give more distinct separate peaks than those of [W]. According to chemical analysis, [U] contains a small amount of residual Zn^{2+} and Cl^- ions, and [W], no residual ion. However, according to the X-ray results and chemical analysis, there are no difference in crystal structure and hydrogen contents between [U] and [W]. This suggests that the endothermic peak at near 710 °C and the exothermic peaks at higher temperature of [U] should be due to residual ions.

As has been reported[6,7] Type-I is decomposed by vacuum heating to the nonstoichiometric oxide with the rhombic MoO_3 structure by evolution of H_2O.

$$H_{0.30}MoO_3 \longrightarrow H_{0.21}MoO_{2.95}{}^{22)}$$

$$\longrightarrow H_{0.06}MoO_{2.88}{}^{23)} \longrightarrow MoO_{2.85}{}^{23)}$$

It is very important to know the decomposition of bronzes in air. As mentioned above, there are no differences in the crystal structure and hydrogen contents between [U] and [W]; however, [U] gives more distinct exothermic peaks than does [W]. Type-I treated at about 150 °C shows the original orthorhombic crystal structure, but that treated at about 330 °C shows the rhombic MoO_3 structure. The compositions of all phases heated at the temperature before and after exothermic peaks (marked by arrows (⟶) in Fig. 5) are shown in Table 1. This result suggests that the hydrogen molybdenum bronze changes successively from a bronze with a higher hydrogen content to one with a lower hydrogen content upon heating: Type-IV⟶Type-III⟶Type-II⟶Type-I⟶MoO_3.

The weight loss of samples can be calculated from TG curves. [U] gives a clear phase separation, though it contains a small amount of residual Zn^{2+} and Cl^- ions. It is therefore not reasonable to obtain gravimetric results. The total weight losses are obtained from the TG results of [W] by substracting the adsorbed water molecules (Table 2). Under vacuum heating, the decomposition of Type-I takes place by an evolution of H_2O. Usually, the decomposition of a bronze can occur by the following two ways.

$$H_xMoO_3 \longrightarrow \frac{x}{2} H_2 + MoO_3 \qquad (1)$$

and

$$H_xMoO_3 \longrightarrow \frac{x}{2} H_2O + MoO_{3-x/2} \qquad (2)$$

Table 2. Weight Loss of Bronzes

x	Weight loss/%		
	H_2	H_2O	Observed
0.21	0.15	1.31	0.40
0.91	0.63	5.65	0.89
1.55	1.06	9.59	1.38
1.90	1.30	11.73	1.29

The weight loss can be lead to the conclusion if the decomposition should proceed by Eq. 1 or 2. Since the hydrogen contents of Type-I, Type-II, Type-III, and Type-IV were determined to be x=0.21, 0.91, 1.55, and 1.90, respectively, the theoretical weight losses were calculated from the above equations (Table 2). Comparing these results, the observed weight loss from TG is very close to the theoretical weight loss calculated from Eq. 1. This means that the bronzes decompose upon heating in air by the evolution of H_2. DTA and X-ray results also support the idea that the decomposition of bronzes change from a higher hydrogen content to a lower hydrogen content. It is therefore reasonable to conclude that the bronzes decompose in air through Eq. 1 as follows:

$$\text{Type IV} \xrightarrow[\text{ca. } 47\,°\text{C}]{\overset{H_2}{\uparrow}} \text{Type III} \xrightarrow[\text{ca. } 91\text{—}99\,°\text{C}]{\overset{H_2}{\uparrow}} \text{Type II}$$

$$\xrightarrow[\text{ca. } 123\text{—}131\,°\text{C}]{\overset{H_2}{\uparrow}} \text{Type I} \xrightarrow[\text{ca. } 149\text{—}157\,°\text{C}]{\overset{H_2}{\uparrow}} MoO_3$$

Precise thermal studies are in progress.

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22) Type I, orthorhombic bronze, with the lowest hydrogen content.

23) Isomorphous with the rhombic MoO_3 structure.