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Structural and Compositional Changes of Blue Orthorhombic Hydrogen Molybdenum Bronze, $H_{0.30}MoO_3$, by Vacuum Heating and Catalytic Activity for 1-Butene Isomerization

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Orthorhombic bronze, $H_{0.30}MoO_3$, was decomposed by vacuum heating to $MoO_{2.86}$ with a rhombic MoO_3 structure. The surface area increased slightly with the increase in the rhombic structure in which vacancies were produced. An approximate linear relationship was found between the catalytic activity of 1-butene isomerization and the hydrogen content(x) in the samples which were treated in air at 65 °C or *in vacuo* below 220 °C. On the other hand, the activity above 220 °C increased with the formation of vacancies.

Molybdenum bronzes (formulated as H_xMoO_3) are obtained from the reduction of MoO_3 by atomic hydrogen.[1—5] Four distinct phases are found in the range $0<x\leqq 2.0$[4] and the homogenieties of these phases are as follows; (i) blue orthorhombic; $0.23<x<0.4$, (ii) blue monoclinic; $0.85<x<1.04$, (iii) monoclinic; $1.55<x<1.72$, and (iv) green monoclinic; $x=2.0$.

These bronzes were expected to be hydrogen reservoirs and interest, therefore, was centered on their catalytic properties. Sermon and Bond[6] have reported that hydrogen in 1% $Pt/H_{1.6}MoO_3$ was useful for 1-pentene hydrogenation. Marcq *et al.*[7] studied the catalytic hydrogenation reaction of ethylene on the red monoclinic bronze, $H_{1.6}MoO_3$, obtained from Pt-supported MoO_3 by hydrogen spillover and confirmed that the atomic hydrogen in the bronze was active for the catalytic hydrogenation of ethylene.

The authors studied the behavior of hydrogen in the blue orthorhombic bronze, $H_{0.30}MoO_3$, by thermogravimetry[8] and by the TPD method.[9] They confirmed that the bronze decomposed to $MoO_{2.86}$, a nonstoichiometric compound with the rhombic MoO_3 structure, in three steps when the bronze was heated under a vacuum of 10^{-4} Torr† and in a helium atomosphere.

Using proton NMR studies,[10] the authors found no difference in the behavior of the protons in the untreated and treated samples and indicated that the environments surrounding the protons did not change throught heat treatment.

In the present work, the catalytic activity for 1-butene isomerization over the bronzes was studied. The structural and compositional changes of the bronzes after these treatments were also studied. The authors tried to reveal the relationship between the catalytic activity and the hydrogen content(x) or between that and the structural and compositional changes of the samples.

Experimental

The preparation and identification of $H_{0.30}MoO_3$ used in the present experiments were described previously.[8—10] Samples, having various hydrogen contents, were prepared by heating the bronze *in vacuo* or in air. The structural and compositional changes of the samples were studied by X-ray powder diffractometry and infrared spectrophotometry.

1-Butene from Takachiho Kagaku Co. Ltd. was purified by repeated distillation *in vacuo*. The purity was confirmed by gaschromatography to be higher than 99%. A closed circulating system connected to a conventional vacuum line was used for isomerization of the 1-butene. The reaction mixtures were analyzed for each fixed time using the gaschromatograph with a coloum of 2,5-dimethylsulforan (DMS).

The surface area was determined by the BET method.

Results and Discussion

Structural and Compositional Changes of $H_{0.30}MoO_3$. Figure 1 shows the X-ray diffraction pattern of the samples heated at various temperatures *in vacuo* for 60 min. The sample heated at 238 °C showed an X-ray diffraction pattern due to the original orthorhombic structure. However, the pattern due to the rhombic structure appeared on samples treated at 297 and 349 °C. This result means that these samples consist of a mixture of the orthorhombic and rhombic structures. While the sample heated *in vacuo* at 398 °C showed only the X-ray patterns due to the rhombic structure,

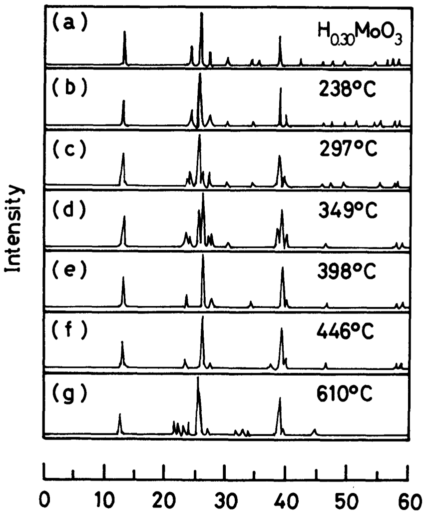

Fig. 1. X-ray diffraction patterns of the blue orthorhombic bronze, $H_{0.30}MoO_3$(a), and the samples treated at 238 °C(b), 297 °C(c), 349 °C(d), 398 °C(e), 446 °C(f), and 610 °C(g).

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† 1 Torr ≈ 133.322 Pa.

and the sample heated at 610 °C showed patterns due to mixture of the rhombic MoO_3 and Mo_4O_{11} structures.

As mentioned above, the samples treated at 297 and 349 °C were mixtures of orthorhombic and rhombic structures. The ratio of the orthorhombic to rhombic components was obtained to be 0.76/0.24 (297 °C) and 0.38/0.62 (349 °C), respectively. As the minimum phase limit of the orthorhombic structure was x=0.21 in the present work, the ratio can also be calculated from thermogravimetric data. The ratio was 0.80/0.20 (297 °C) and 0.35/0.65 (349 °C), respectively. These values are in very good agreement with each other. This suggests that the ratio obtained from the thermogravimetric data is easier to use than that obtained from the X-ray results. The sample in which the hydrogen content was x=0.06 showed only a pattern due to the rhombic structure. During vacuum heating, the only gas liberated from the sample was H_2O. No other gas was detected using a quadrupole gas analyzer. This result suggests that the hydrogen atoms in the samples reacted with lattice oxygen to produce H_2O. The bronze with the lowest hydrogen content (x=0.21) transformed to a compound with a hydrogen content of x=0.06 and finally to a nonstoichiometric compound with a rhombic MoO_3 structure, which contains no hydrogen atoms. These results lead to the conclusion that vacancies should be produced in the samples during the evolution of H_2O under vacuum heating. These changes are formulated as follows;

$$\begin{aligned} H_{0.30}MoO_3 &\xrightarrow{\approx 287^{\circ}C} H_{0.21}MoO_{2.95}{}^{*} \\ &\xrightarrow{\approx 390^{\circ}C} H_{0.06}MoO_{2.88}{}^{**} \\ &\xrightarrow{\approx 446^{\circ}C} MoO_{2.86}{}^{***} \\ &\xrightarrow{\approx 610^{\circ}C} MoO_3 + Mo_4O_{11} \end{aligned}$$

*; Orthorhombic bronze with the lowest hydrogen content.

**; Isomorphous with rhombic MoO_3.

***; Nonstoichiometric compound with the rhombic MoO_3 structure.

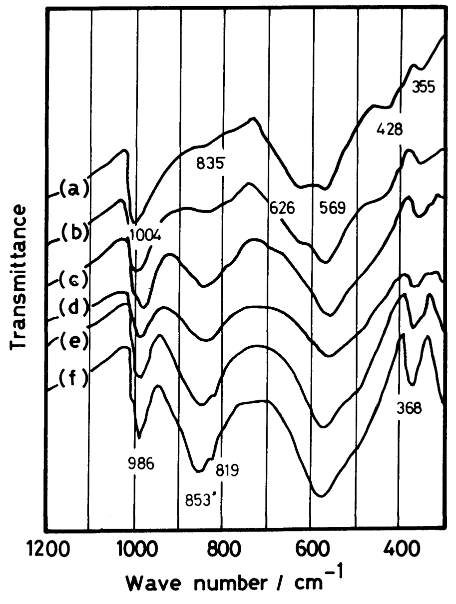

Fig. 2. IR spectra of the blue orthorhombic bronze, $H_{0.30}MoO_3$(a), and the samples treated at 238 °C(b), 297 °C(c), 349 °C(d), 398 °C(e) and 446 °C(f).

Figure 2 shows the IR spectra of a sample treated at various temperatures for 60 min under a vacuum of 10^{-4} Torr. The orthorhombic bronze showed bands at 1004, 626, 569, and 355 cm^{-1}. These bands agree well with those reported by Schroder and Weizel.[3] The intensities of the bands at 1004, 626, and 428 cm^{-1} gradually decreased during vacuum heating. On the other hand, the bands at 986, 853, 819, 569, and 368 cm^{-1} appeared after heating at 297 °C and the intensities of these bands gradually increased by further heating. According to the X-ray results mentioned above, the samples treated at 297 and 398 °C were mixtures of orthorhombic and rhombic structures and the sample treated at 398 °C was a nonstoichiometric compound with a rhombic MoO_3 structure. These facts suggest that a compound with a rhombic MoO_3 structure shows bands at 986, 853, and 819 cm^{-1}. These bands are a little lower than those at 998, 878, and 820 cm^{-1} in literatures.[11–13] This difference may be considered as a result of nonstoichometry. According to Nakamoto[12] and Feraro,[13] as shown in Fig. 3 (A1 and A2), the bands at 986, 853, and 819 cm^{-1} can be assigned to Mo=O(1), Mo–O(3,3′)–Mo, and Mo–$\underset{\underset{\text{Mo}}{|}}{\text{O}}$(2,2′)–Mo, respectively. Figure 3 also shows the coordination of the oxygen atoms arround the molybdenum atom in MoO_3 (B) and in the orthorhombic bronze(C). In MoO_3, the bond lengths of Mo–O(2′), Mo–O(3), and Mo–O(3′) are 1.95, 2.25, and 1.73 Å, respectively. On the other hand, in orthorhombic bronze, that of Mo–O(2′), Mo–O(3), and Mo–O(3′) is 1.96 Å. That is, by an insertion of atomic hydrogen into MoO_3, the bond length of Mo–O(3) in MoO_3 is shortened to 1.96 Å in the orthorhombic bronze and that of Mo–O(3′), longthened to 1.96 Å. However, that of Mo=O(1) showed no difference between the MoO_3 and the orthorhombic bronze. The band at 1004 cm^{-1} of the orthorhombic bronze is assumed to correspond to that at 998 cm^{-1} of the rhombic MoO_3. On the other hand, any band corresponding to the bands at 878 and 820 cm^{-1} due to MoO_3 was not observed in orthorhombic bronze. However, as atomic hydrogen was removed by vacuum heating, the bands at 986 and 819 cm^{-1} appeared and the intensities increased. These results suggest that, though small bands due to Mo–O(3,3′)–Mo and Mo–$\underset{\underset{\text{Mo}}{|}}{\text{O}}$(2,2′)–Mo in the orthorhombic bronze should be expected, they were not observed.

Changes in Surface Area. The changes in the surface areas of the samples treated under vacuum

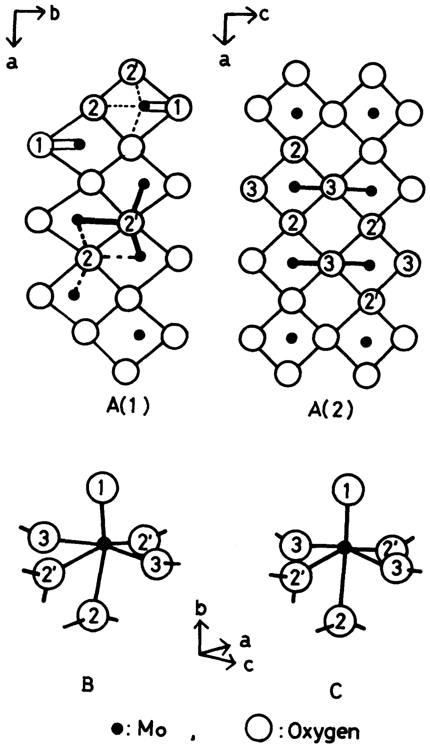

Fig. 3. Schematic model of MoO_3(A1,A2) and coordination of oxygen atoms around the molybdenum atoms in MoO_3(B) and in the bronze(C).

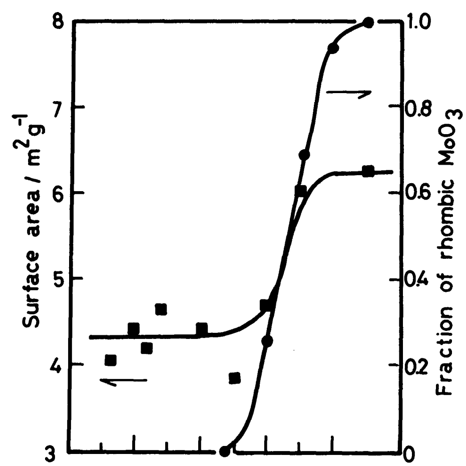

Fig. 4. Changes of the surface area and the fraction of the rhombic MoO_3 structure in the samples after vacuum heating.

heating at various temperatures are shown in Fig. 4. No large change was observed below 300 °C, but the area increased slightly to a constant value at 360 °C. The fraction of the rhombic structures in the samples is also shown in Fig. 4. The change in the fraction agrees well with that for the surface area. As mentioned above, isomorphous and nonstoichiometric compounds with rhombic structures have many vacancies produced by the reaction of lattice oxygen with hydrogen. Therefore, the increase in the surface area may be caused by an increase in the rhombic structure which has vacancies.

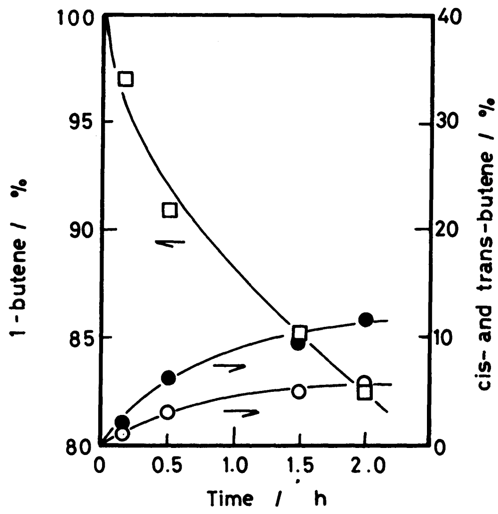

Fig. 5. Isomerization of 1-butene over $H_{0.24}MoO_3$ at 65 °C.
□: 1-Butene, ●: *cis*-2-butene, and ○: *trans*-2-butene.

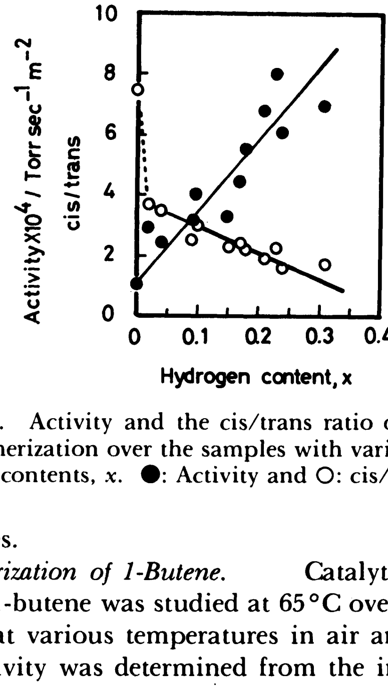

Fig. 6. Activity and the cis/trans ratio of 1-butene isomerization over the samples with various hydrogen contents, *x*. ●: Activity and ○: cis/trans ratio.

Isomerization of 1-Butene. Catalytic isomerization of 1-butene was studied at 65 °C over the bronzes treated at various temperatures in air and *in vacuo*. The activity was determined from the initial rate of decrease of 1-butene, which was divided by the surface area of the catalyst. The skeletal isomerization could not be observed. No other gasous hydrocarbons other than butenes were detected in the reaction mixtures under the present experimental conditions. Figure 5 shows typical changes of butenes with time over $H_{0.24}MoO_3$ at 65 °C. The *cis*-2-butene is predominantly formed.

The samples with various hydrogen contents were obtained by heating the bronze in air at 65 °C for various heating times. The activities of 1-butene isomerization were plotted against *x*, as shown in Fig. 6. A linear relationship exists between the activity and *x*. The activity of commercial MoO_3 was about 1/500 of the MoO_3 obtained from a bronze of which hydrogen was completely removed by heating in an oxygen

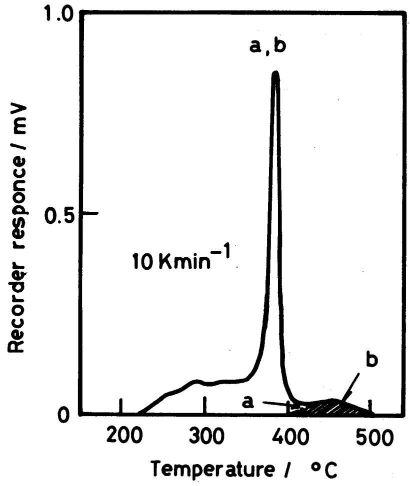

Fig. 7. TPD spectra of $H_{0.24}MoO_3$(a) and the sample after exposure to 1-butene.

atomosphere. Further, when the atomic hydrogen of the bronze was replaced by alkali metal ions, such as potassium ions, the activities of the alkali metal bronzes decreased markedly. As in the case of the hydrogenation of 1-pentene and ethylene over $H_{1.6}MoO_3$, the above results lead to the conclusion that hydrogen atoms in orthorhombic bronze, $H_{0.30}MoO_3$, are effective for the catalytic isomerization of 1-butene.

Figure 7 shows the TPD spectra of the orthorhombic bronze, $H_{0.24}MoO_3$(a), and the sample(b) after use as a catalyst for 1-butene isomerization. The shaded part is observed only in the spectrum of a used sample. The gas liberated as H_2O was trapped at −60——63 °C. The value of the trapped gas obtained from the used sample was the same as that from the unused sample. This suggested that the area was equal to that of the unused sample. These results suggest that the bronze did not change at all throught the 1-butene isomerization. This leads to the conclusion that the hydrogen atoms in the bronze were effective for the catalytic isomerization of 1-butene. The shaded part is difficult to identify, but may be a strongly adsorbed species of hydrocarbons.

The cis/trans ratios of 1-butene isomerization over the samples were also plotted against x. As shown in Fig. 6, the ratio over MoO_3 obtained from the bronze is high. However, when small amounts of hydrogen is introduced, the ratio decreases steeply at first. Then, it decreased gradually to 1.6—1.7 with an increase in x. The cis/trans ratio at an equilibrium composition of butenes at 65 °C, as calculated from the thermodynamical data,$^{14)}$ was 0.4. In the present work, therefore, the *cis*-2-butene was predominantly formed. It is well known$^{15)}$ that when a solid acid catalyst is used for 1-butene isomerization, the cis/trans ratio is 1—2, while in the case of the solid base catalyst the ratio is more than 2. Considering the facts that the cis/trans ratios linearly decreased to 1.6—1.7 over the samples for which x increased, the bronze with small amounts of hydrogens was assumed to act as the solid acid catalyst.

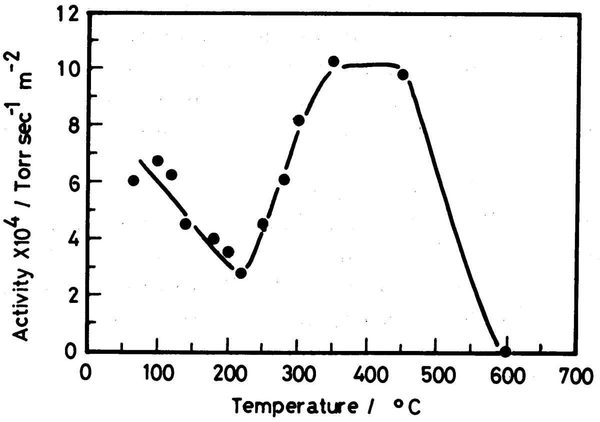

Fig. 8. Effect of evacuation temperature on catalytic activity of 1-butene isomerization.

As hydrogen is involved with the bronze as atoms, it is reasonable that this atomic hydrogen acts as a solid acid catalyst.

Figure 8 shows the change in the activity of the samples which were treated *in vacuo* at various temperatures. The activity decreased linearly up to 220 °C, increased monotonously to a maximum value at 350 °C, and decreased sharply to nearly zero from 450 to 600 °C. The activity below 220 °C decreases linearly with a decrease in the hydrogen content of the samples without any structural change. In addition to the results mentioned above, this result suggests that the activity depends on the hydrogen atoms.

The activity increased from 220 to 350 °C and reached a constant value. In these temperature ranges, $H_{0.21}MoO_{2.95}$ decomposed rather rapidly to $H_{0.06}MoO_{2.88}$ with the rhombic MoO_3 structure with the formation of vacancies, which caused an increase in the surface area. The change from $H_{0.06}MoO_{2.88}$ to $MoO_{2.86}$ showed no significant change in the structure and in the surface area. Considering the above results, it is reasonable to conclude that the catalytic activity at this temperature range(220—350 °C) is attributed to the vacancies produced in the samples.

In this case, the cis/trans ratio on the samples treated below 220 °C varied with x, while the ratio above 220 °C was nearly constant at 1.4—1.7. As reported previously,$^{15)}$ these ratios fell just in those ranges on the solid acid catalysts. As mentioned above, the activity for the isomerization of 1-butene above 220 °C is due to the vacancies produced in the bronze which show a reduced state. Considering the above results, it can be said that the activity above 220 °C results from the vacancies formed during treatment and that these vacancies act as a solid acid-like catalyst. A precise investigation is in progress.

The activity decreased markedly from 450 to 600 °C. From the X-ray and thermogravimetric results, the sample was confirmed to be a mixture of MoO_3 and Mo_4O_{11}. $MoO_{2.86}$, the nonstoichiometric compound with a rhombic structure, is converted to the stoichiometric MoO_3 and Mo_4O_{11}. The catalytic activity of 1-butene isomerization on MoO_3 and Mo_4O_{11} is very small. Therefore, these results lead to the conclusion that the decrease in the activity can be attributed to the existence of the stoichiometric MoO_3 and Mo_4O_{11}.

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