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Hydrogen Insertion on Alkali Metal Decamolybdates by Spillover

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A hydrogen-insertion process by spillover on alkali metal decamolybdates was investigated in situ. Hydrogens were inserted, leading to the formation of OH groups. The insertion induced dehydration (release of the crystallization water of the molybdates), which resulted in distortions in the Mo–O framework. The dehydration behaviour varied depending on the kinds of decamolybdates or the manners in which the decamolybdates have crystallization-water species. Furthermore, structural changes of the resultant compounds with heat-treatments in N_2 were also investigated. It was then confirmed that these compounds could become starting materials, leading to the formation of alkali metal molybdenum bronzes at lower temperatures, ca. 200 K below those used in ordinary syntheses.

Alkali metal decamolybdates, $M_2Mo_{10}O_{31}\cdot nH_2O$, have the interesting structure which consists of double chains of edge-sharing MoO_6 octahedra linked by sharing corners, as shown in Fig. 1.[1,2] The structure exhibits a three-dimensional network with wide one-dimensional tunnels, where alkali-metal ions are located. Such wide one-dimensional tunnels allow rich intercalation chemistry and provide some specific reaction fields, low-dimensional properties, such as ion conductivity. These compounds are thus important subjects of materials chemistry.

From two points of views we have been interested in hydrogen insertion on them. The first one concerns the hydrogen-insertion behavior and/or the resultant materials. We hope to know how hydrogen is inserted and what kinds of phases are formed. Such information is of interest in materials science. The resultant phases may thus be functional materials, such as good proton conductors or low-dimensional ionic conductors which can be used in batteries, fuel cells, chemical sensors, supercapacitors, and so on. The second one is related to a new synthesis method for materials. We have proposed synthesis routes in which non-stoichiometric compounds having wide homogeneity ranges are used as starting materials. Such non-stoichiometric compounds can take various compositions, matched to target materials, within their single-phase ranges. The use of these single-phase compounds as starting materials can reduce any unnecessary mass transport which takes place in the usual syntheses starting from mixtures. We used these routes to synthesize alkali metal molybdenum bronzes which exhibit interesting properties.[3–6] We then confirmed lowering of their synthesis temperatures,[7–11] and obtained a phase which had not been previously obtained by the usual synthesis techniques.[12] These results show the effectiveness of such routes. However, we have an insufficient choice of non-stoichiometric compounds to be used as starting materials. It is necessary to enrich the choice. The hydrogen-insertion compounds of alkali decamolybdates are expected to become non-stoichiometric compounds with wide homogeneity ranges, as seen for many hydrogen-insertion compounds.[13] It is therefore needed to test whether these compounds can be used as starting materials.

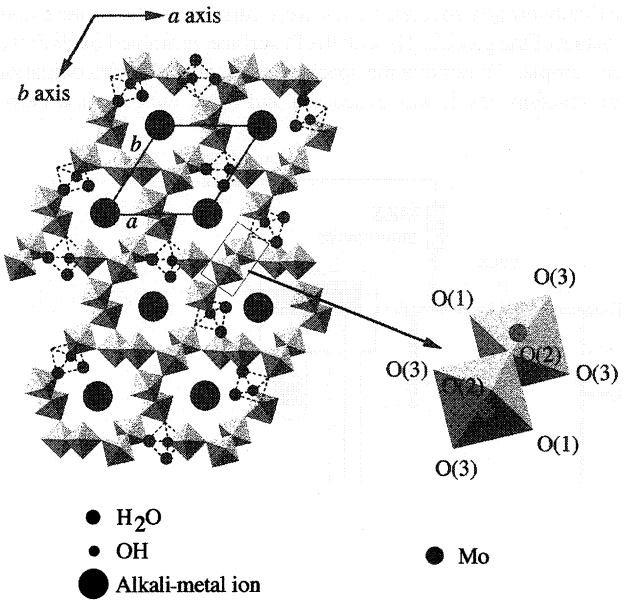

Fig. 1. Schematic model of structure for alkali metal decamolybdates.

We already investigated hydrogen insertion on sodium decamolybdate by chemical reduction with Zn/HCl, and succeeded to insert hydrogen into the decamolybdate framework.[14] However, in that case, Na^+ in the tunnel site was fully exchanged by a proton during the chemical reduction. As a technique to attain hydrogen insertion without removal of the tunnel-site ions, we could think of the spillover technique. Hydrogen spillover was first found by Kuriacose[15] and applied to the hydrogen insertion on MoO_3 by Sermon & Bond[16] and Marcq et al.[17] In the present work we used the technique for hydrogen insertion on decamolyb-

dates instead of chemical reduction. The insertion process was investigated in situ. Then, we obtained many findings for the process, such as dehydration (release of crystallization water of the decamolybdates) induced by hydrogen insertion, the dependence of the dehydration behavior on kinds and amounts of crystallization-water species in decamolybdates, and some interesting differences between the hydrogen-insertion behaviors by hydrogen spillover and by chemical reduction. The details will be reported. The findings concerning the second point of view will also be presented briefly.

Background: Crystallization Water in Alkali Metal Decamolybdates. The ideal composition of alkali metal decamolybdate, $M_2Mo_{10}O_{31}\cdot 5H_2O$, has been given by Krebs and Paulat-Böschen.[1] The five water molecules have been known to be in the neighborhood of the vacant molybdenum position, which exists randomly at one of the six equivalent Mo positions in the unit cell, and to be constituted of two (0.2 H_2O/Mo) coordination-water molecules bonded to Mo (named Mo–CW), two (0.2 H_2O/Mo) lattice-water molecules (named LW), and one (0.1 H_2O/Mo) OH group (named OHW), as shown in Fig. 1. However, in recent studies,[18—20] it was revealed that only lithium and potassium decamolybdates had formulae rather close to the ideal one. The formulae of other decamolybdates largely deviate from it. For example, the sodium salt has one (0.1 H_2O/Mo) extra water molecule, which is coordinated directly to the alkali metal cation (named A–CW), other than the five water molecules.[18—20] On the other hand, the rubidium and cesium salts have lower water contents than the ideal one, because of a huge lack of LW due to steric effects of the large alkali cations, which locate on the tunnel sites (Fig. 1).[19,20]

Experimental

Materials. Three kinds of alkali metal decamolybdates (Na, K, and Cs), which have different manners to form crystallization water (as shown below) were used as host materials for hydrogen insertion. The alkali metal decamolybdates were prepared by heating acidified A_2MoO_4 solutions.[2,20] They were confirmed to be pure by X-ray diffraction (XRD). Their compositions were $Na_2Mo_{10}O_{31}\cdot 6H_2O$ (Mo–CW, 0.20; LW, 0.20; OHW, 0.10; A–CW, 0.10 H_2O/Mo), $K_{1.7}Mo_{10}O_{30.9}\cdot 4.4H_2O$ (Mo–CW, 0.20; LW, 0.14; OHW, 0.10 H_2O/Mo), and $Cs_{1.8}Mo_{10}O_{30.9}\cdot 3.4H_2O$ (Mo–CW, 0.20; LW, 0.04; OHW, 0.10 H_2O/Mo), respectively.[19,20]

Commercial-grade hydrogen gas (Sumitomo Seika, zero-A grade) was purified by passing through a cold trap, soaked in liquid N_2, and used for the spillover procedure. A commercial grade of platinum (Pt) black (Wako pure chemicals, practical grade) was used without further purification.

Hydrogen Spillover Procedure. Hydrogen insertion by spillover was performed on the apparatus shown in Fig. 2. The apparatus consisted of two parts (one was for gas introduction and the other for a spillover reaction) divided by stop-cock A, and was equipped with a MKS instruments inc. baratron 227AA capacitance manometer, a Cahn electronic microbalance, and a rotary pump. First, 2—3 g of the decamolybdate and 1 wt% amount of Pt black were mixed well with a mortar and a pestle. Then, 200 mg of the mixture in a Pyrex glass bucket was put on the microbalance and used as a starting sample. After setting the sample the reaction vessel was evacuated. Evacuation led to a large weight loss due to the release of water species in the sample. However, when the evacuation was stopped, the sample weight became constant within 30 min, and showed no weight change without further evacuation or hydrogen introduction. After the weight became constant, hydrogen gas (15—80 Torr, 1 Torr = 133.322 Pa) was introduced to the reaction part. Then, the insertion process was investigated in situ by monitoring changes in the vessel (hydrogen) pressure and the sample weight with the capacitance manometer and the microbalance, respectively. During the experiment, room temperature was controlled at about 293 K with an air conditioner. A blank test was performed using 2 mg of Pt black, which would be contained in 200 mg of the sample mixture; no changes were observed in the hydrogen pressure or the sample weight.

After the spillover procedure, the sample was taken out from the vessel and investigated by chemical and thermogravimetric-differential thermal (TG-DTA) analyses, powder XRD, atomic-absorption and infrared (IR) spectroscopies, proton-nuclear magnetic resonance (NMR), and/or scanning electron microscopy (SEM), if necessary. Upon removing the sample into the air atmosphere, active hydrogen species, which were formed on the sample upon contact of the gaseous H_2 with the Pt surface, promoted oxidation of the sample. To remove the species and to minimize the oxidation, the reaction vessel was evacuated and filled with N_2 just before

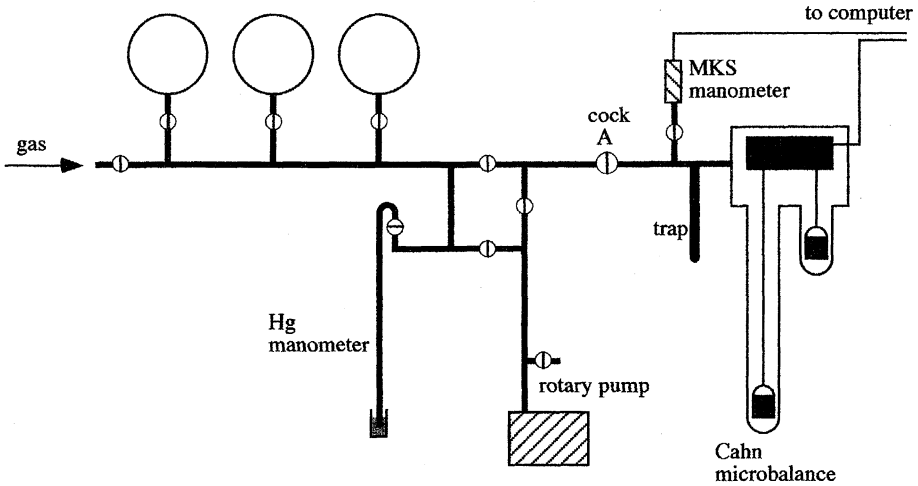

Fig. 2. Apparatus for the spillover procedure.

removing the sample.

Characterization of Materials. XRD measurements were performed on a Rigaku RINT 1200M diffractometer with Cu $K\alpha_1$ (λ = 1.54056 Å) radiation (40 kV, 40 mA). IR spectra were measured on a Perkin Elmer 1600 and/or a Perkin Elmer system 2000 FT-IR spectrometer. For IR measurements, samples were mixed with KBr and pressed into pellets. The water content of the sample was estimated from TG results obtained both in air and in N_2 at a heating rate of 10 K min^{-1} with a Mac Science TG-DTA 2010S system. The Na, K, Cs, and Mo contents of the sample were measured on a Hitachi 180-80 atomic-absorption spectrometer with the 589.0, 766.5, 852.1, and 313.3 nm lines, respectively. The Mo^{5+} content of the sample was determined by the reducing power titration.[21] SEM images were obtained using a JEOL JXA 8900 microanalizer.

Heat-Treatment Procedure. On the TG-DTA system the hydrogenated (hydrogen-inserted) sample was heated up to desired temperatures at a heating rate of 10 K min^{-1} and then cooled down to room temperature in N_2. After the treatment the sample was investigated by XRD.

Results

Hydrogen Insertion. Figure 3 shows the typical time-course of the vessel (hydrogen) pressure and sample weight during the spillover procedure for sodium decamolybdate. The event time of hydrogen introduction was drawn to be zero in the figure. The weight loss observed before time 0 is ascribed to the release of the water species in the sample by evacuation. The vessel pressure decreased exponentially after the introduction. Such a pressure change is reasonable for the insertion reaction. However, the weight change was slightly complicated. That is, it reached to a small maximum just after the introduction, and then decreased exponentially. The large exponential decrease in weight is rather attributed to dehydration. It is suggested that dehydration is induced by hydrogen introduction, or hydrogen insertion into the sample, because no weight change is observed without the introduction (see the explanation of the spillover procedure in the experimental section and the plateau just before time 0 on the sample-weight curve in Fig. 3). To investigate the relation between the hydrogen- and water-contents of the sample, we estimated these two contents from the pressure and weight changes. The hydrogen uptake was obtained from the decrease in the pressure, while the amount of released water was obtained from the sample-weight changes by subtracting the contribution (weight gain) due to the estimated hydrogen uptake. These results showed an exponential increase in the hydrogen uptake and an exponential decrease in the water content. A plot of the water content (molar ratio H_2O/Mo) vs. the hydrogen uptake (molar ratio H/Mo) is shown in Fig. 4. Because the sample composition during hydrogen insertion can be written as $H_{10x}Na_2Mo_{10}O_{31}\cdot nH_2O$, the values n/10 and x are used in the figure as the water- and hydrogen-contents, respectively. The figure shows a linear relation between the two contents, supporting that hydrogen insertion induces dehydration, except for the region $x <$ ca. 0.3. To confirm the relation further, we also analyzed the two contents of the sample directly. The samples at various insertion stages were taken out from the reaction vessel and investigated by TG-DTA and chemical analysis. The Na content of the sample was also analyzed by atomic-absorption spectroscopy. As regards the Na content no change was observed during the spillover procedure. Figure 5 shows the results for the hydrogen and water contents, together with those for the chemically reduced samples.[14] The sample hydrogenated by spillover gives a linear relation similar to that in Fig. 4, although the relation can be seen even at low hydrogen-contents in this case. According to a comparison between Figs. 4 and 5, the samples taken out into air atmosphere exhibit slightly lower hydrogen and slightly higher water contents than those estimated in situ. These differences indicate that the samples are slightly oxidized when they are dealt with in the air atmosphere, and that the water content depends on the atmosphere (probably water vapor pressure in the atmosphere). For the water content, it should be noted that samples hydrogenated by spillover take lower values than those prepared by the chemical reduction (Fig. 5).

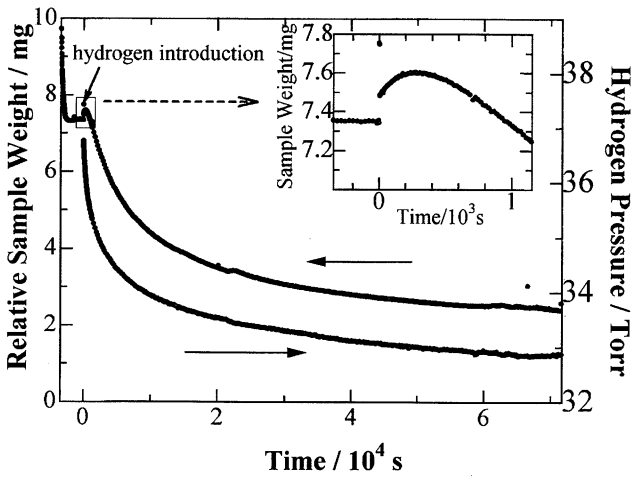

Fig. 3. Time-course of vessel pressure and sample weight during hydrogen insertion on sodium decamolybdate by spillover. An initial hydrogen pressure of 37 Torr was used.

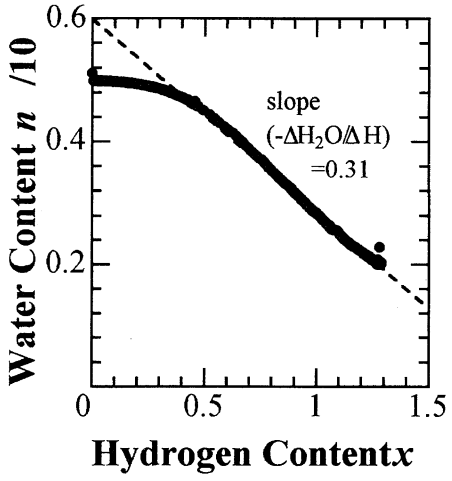

Fig. 4. The changes of the water content n/10 ([H_2O/Mo]) against the hydrogen uptake x ([H/Mo]) for the sample ($H_{10x}Na_2Mo_{10}O_{31}\cdot nH_2O$) during the spillover (in situ).

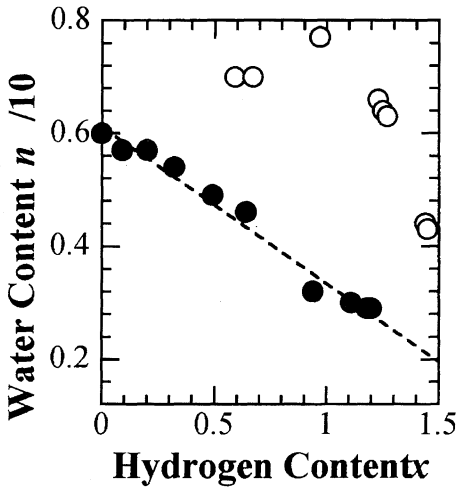

Fig. 5. The changes of the water content $n/10$ ([H_2O/Mo]) against the hydrogen uptake x ([H/Mo]) for the hydrogen-inserted sodium decamolybdates, dealt in ambient atmosphere after the hydrogen insertion: ●, by spillover; ○, by the chemical reduction.

Furthermore, we investigated the dependence of the hydrogen-insertion behavior on the initial water content (the content at time 0). The content of the sample was varied (in the range $4 < n < 5$ for sodium decamolybdate) by arranging the evacuation time before hydrogen introduction. Linear relations with almost the same slope ($\equiv -\Delta H_2O/\Delta H$) were observed for all samples with various water contents. The slope was 0.31. Then, the final water content after hydrogen insertion was almost constant and about 0.2 H_2O/Mo, while the final hydrogen uptake depended on the initial water content. The relation between the hydrogen uptake and the hydrogen pressure was also investigated. The final hydrogen uptake increased with increasing hydrogen pressure, and we obtained a hydrogenated sample with $x = 1.5$, which corresponded to the maximum obtained by chemical reduction[14] at a pressure of 80 Torr.

Similar linear relations between the hydrogen- and water-contents were also observed for potassium and cesium decamolybdates. The slopes ($-\Delta H_2O/\Delta H$, obtained in situ) were 0.28 for potassium decamolybdate and 0.15 for cesium decamolybdate. The water contents of fully hydrogenated samples were 0.08 and 0.12 H_2O/Mo for potassium and cesium decamolybdates, respectively.

Hydrogen-Inserted Materials. Figure 6 shows the XRD patterns of the hydrogenated (hydrogen-inserted) sodium decamolybdates. There seems to be two phases in the figure. These phases are, respectively, observed as single phases in the regions $x \leq 0.3$ and $x \geq 1.3$, and named phases I and II. From their XRD patterns it is apparent that phase I exhibits a hexagonal structure similar to that of the original decamolybdate and phase II also seems to retain the Mo–O framework of the molybdate. However, it should be noted that phase II shows rather broad XRD peaks, indicating a largely distorted structure or small particle size. According to a SEM observation, no significant difference in the particle size was observed between the samples $H_3Na_2Mo_{10}O_{31}\cdot 5.4H_2O$ (phase

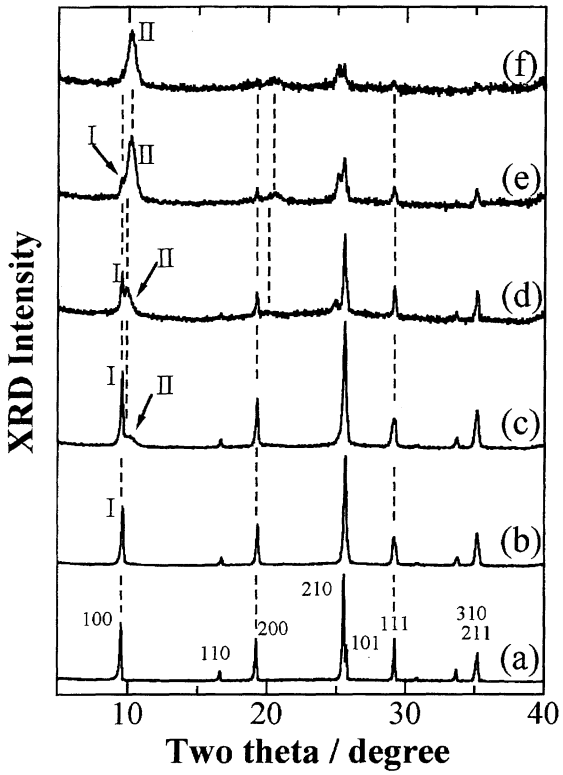

Fig. 6. XRD patterns of the hydrogen-inserted sodium samples ($H_{10x}Na_2Mo_{10}O_{31}\cdot nH_2O$): $x = 0$, $n = 6.0$ (a); $x = 0.3$, $n = 5.4$ (b); $x = 0.5$, $n = 4.9$ (c); $x = 0.7$, $n = 4.6$ (d); $x = 1.1$, $n = 3.0$ (e); and $x = 1.3$, $n = 2.4$ (f).

I, $x = 0.3$, Fig. 6b) and $H_{13}Na_2Mo_{10}O_{31}\cdot 2.4H_2O$ (phase II, $x = 1.3$, Fig. 6f). Thus, the broad peaks are due to its largely distorted structure. According to the figure, the positions of the 100 and 200 reflections shift to the higher degree side as the hydrogen content increases, while that of the 111 reflection, slightly to the lower side. Similar shifts were also observed for samples heavily hydrogenated by chemical reduction.[14] A detailed interpretation of the observed XRD peaks of both samples showed that these shifts resulted from a shortening of the a ($= b$) axis and an elongation of the c-axis (the ca. 25° peak, newly observed for the samples with larger x values, is assigned to the 101 reflection). Then there is an apparent difference between the phase-change behaviors due to spillover and chemical reduction. A sample prepared by spillover becomes a mixture of the two phases in the region $0.3 < x < 1.3$, while that by chemical reduction becomes a single phase in all regions of $0 \leq x \leq 1.5$.[14]

Figure 7 shows the IR spectra of hydrogenated sodium decamolybdates. Five peaks at 970, 910, ca. 720, 629, and 520 cm^{-1} are observed in the spectrum of the original decamolybdate ($x = 0$). The two bands above 900 cm^{-1} can be ascribed to stretching vibrations of the terminal oxygen (Mo=O(1), Fig. 1), while the other three below 750 cm^{-1} are related to vibrations of single Mo–O bonds in the Mo–O–Mo or the Mo–OH. By hydrogen insertion, the peaks above 900 cm^{-1} shift to the lower wavenumber side, reducing their relative intensities. Being accompanied by a reduction of these peaks, the band at around 720 cm^{-1} increases in in-

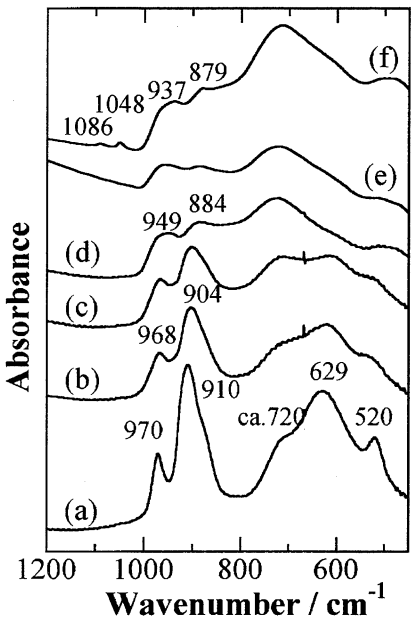

Fig. 7. IR spectra of the hydrogen-inserted sodium samples ($H_{10x}Na_2Mo_{10}O_{31}\cdot nH_2O$): $x = 0$, $n = 6.0$ (a); $x = 0.3$, $n = 5.4$ (b); $x = 0.5$, $n = 4.9$ (c); $x = 0.7$, $n = 4.6$ (d); $x = 1.1$, $n = 3.0$ (e); and $x = 1.3$, $n = 2.4$ (f).

tensity. These changes can be ascribed to the formation of OH species by an attachment of the inserted hydrogen to the terminal oxygen. Similar changes were also observed for samples hydrogenated by chemical reduction.[14] Moreover, the spectrum of the sample with $x = 1.3$ shows two weak peaks at 1048 and 1086 cm^{-1}. These bands have also been observed in the IR spectra of the hydrogen-insertion compounds of the molybdenum oxide hydrate,[22,23] and can be related to bending vibrations of the Mo–O–H species, which are formed by hydrogen insertion.

The proton-NMR study showed increases in the intensity of the Gaussian peak, which were attributed to the OH species, and decreases in the intensity of the Pake doublet-like peaks, which were due to the OH_2 species, as the hydrogen content increased. These results support the formation of the OH species and dehydration induced by hydrogen insertion. Similar XRD, IR, and NMR results were also observed for the hydrogenated potassium and cesium decamolybdates.

Heat-Treatments of Hydrogenated Materials. As mentioned above, the hydrogenated alkali metal decamolybdates are expected to be starting materials for the syntheses of alkali metal molybdenum bronzes. As a stable sodium molybdenum bronze prepared at atmospheric pressure, only the purple bronze, $Na_{0.9}Mo_6O_{17}$ (with ratios of 0.15 Na/Mo and 0.49 Mo^{5+}/Mo), has been known.[3,4] In the present work hydrogenated sodium decamolybdate with 0.49 Mo^{5+}/Mo could not be prepared as a single phase (Fig. 6). Thus hydrogenated samples with $x = 1.3$, which were obtained as a single phase and having a higher Mo^{5+} content than that of the sodium bronze, were used to test only if the hydrogenated sample could be used as a starting material for bronze synthesis. Figure 8 shows TG-DTA curves in N_2 of hydrogenated

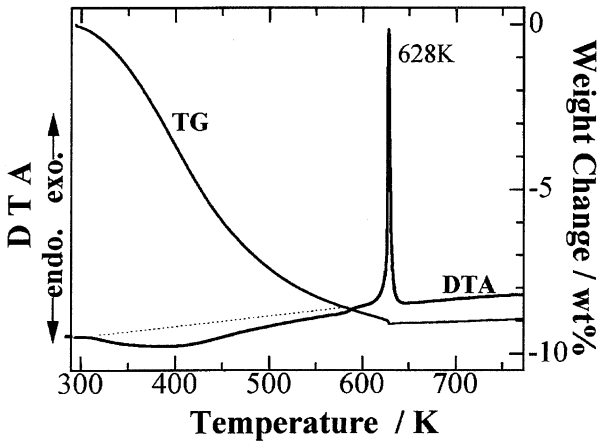

Fig. 8. TG-DTA curves in N_2 of the hydrogen-inserted sodium decamolybdate with $x = 1.3$.

sodium decamolybdate. The DTA curve gives a broad endothermic peak with a large weight loss below 600 K and a sharp exothermic peak with a small weight loss at 628 K. The former (endothermic) peak is attributed to the release of water and/or OH groups in the sample as H_2O; the latter peak seems to result from a drastic change in structure. The structures of the sample before and after the latter peak were investigated by XRD. Figure 9 shows the results. According to the figure, the sample just before the peak is amorphous, while that after the peak is a mixture of the purple bronze and MoO_2. Thus, it is suggested that the sample collapses into an amorphous phase, losing its water- and OH-species, and recrystallizes into the mixture at the peak. It should thus be noted that the purple bronze is formed from the hydrogenated sample at a lower temperature (628 K) by ca. 200 K than the ordinary synthesis temperature (ca. 820 K).[24,25]

In the present work, it was also confirmed that $K_{0.30}MoO_3$ and $Cs_{0.30}MoO_3$ were also formed at ca. 630 K from hydrogenated potassium and cesium decamolybdates, respectively. (The usual synthesis temperature of $K_{0.30}MoO_3$ is ca. 820 K.

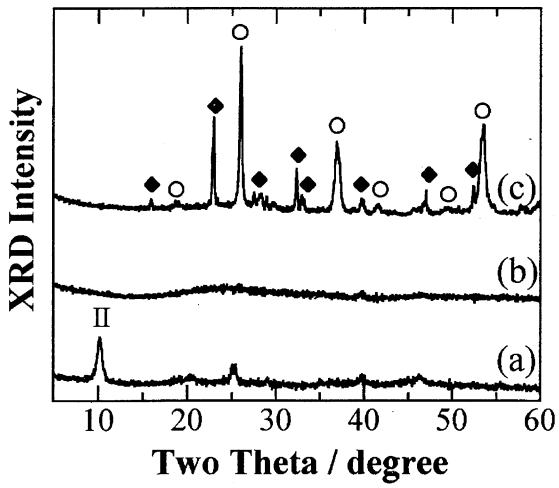

Fig. 9. XRD patterns of the hydrogen-inserted sodium decamolybdate samples (initially with $x = 1.3$): unheated (a), and heated at 560 K (b) and 673 K (c) in N_2. ◆ and ○ indicate $Na_{0.9}Mo_6O_{17}$ and MoO_2, respectively.

$Cs_{0.30}MoO_3$ has never been obtained by the usual methods.)

Discussion

Hydrogen Insertion and Induced Dehydration.

From the IR and NMR results it was revealed that the hydrogen atom, inserted into the decamolybdate, attached to the terminal oxygen O(1) of the Mo–O framework (Fig. 1) to form the OH species. Furthermore, from an in-situ investigation of the insertion process it was found that insertion induced dehydration of the water species originally contained in the decamolybdate.

To understand the dehydration, the data, concerning the water species of the decamolybdates and dehydration behaviour, are summarized in Table 1. The remaining water content in the fully hydrogenated sample is ca. 0.10 H_2O/Mo, except for the case of sodium decamolybdate. OHW is supposed not to be so easily released as LW and Mo–CW,[26,27] and the content (ca. 0.10 H_2O/Mo) agrees with that of OHW in the original samples. As for the sodium salt, which contains A–CW, differing from the other salts, its value of 0.20 H_2O/Mo after full hydrogenation equals to the sum of the amounts of OHW and A–CW. Thus, we suggest that induced dehydration is mainly related to Mo–CW and LW. Regarding the reason why the dehydration is induced by hydrogen insertion, the details have still not been clarified. However, it can be explained to some extent. For Mo–CW, which is directly bonded to a Mo atom, its dehydration is related to changes in the electron configuration of the Mo atom caused by hydrogen insertion. In an extend lattice composed of MO_6 octahedra, which can be seen in the decamolybdates, bonding π and antibonding π^* bands are formed from the surrounding oxygen pπ orbitals and the metal 4d(t_{2g}) orbitals.[28,29] For the $Mo^{VI}O_6$ octahedra, which are in the original decamolybdates, the π band is filled, while the π^* band, empty. The inserted hydrogen atoms transfer their valence electrons to the empty antibonding π^* band. We therefore suppose that electron transfer weakens the bond between the Mo atom and Mo–CW. As for LW, which are not directly bonded to the Mo atom, the changes in the electron configuration are unlikely to cause its dehydration. We think that the release of Mo–CW, which may result in a deficiency, gives rise to distortions in the Mo–O framework. This distortion may induce the dehydration of LW (Fig. 1). Regarding the overall mechanism, Mo–CW is released, leaving a distortion in the Mo–O framework when a hydrogen atom attaches to the terminal oxygen, connected to the same Mo atom to which this coordination water is connected; the resultant distortion gives rise to the simultaneous release of LW in its neighborhood. The following findings (Table 1 and Fig. 6) support this suggestion: 1) the slope ($-\Delta H_2O/\Delta H$) roughly depends on the sum of the amounts of LW and Mo–CW in the original salts, 2) the magnitude of the slope is reasonable for a consideration of the contributions of LW and Mo–CW,[30] and 3) the hydrogenated samples show distorted structures. Then, the deviation from a linear relation between the water- and hydrogen-contens at the initial stage, illustrated in Fig. 4, seems to be related to hydrogen insertion into the sites where neighboring crystallization-water species were lost by evacuation preceding to hydrogen introduction.

Structural Changes Due to Hydrogen Insertion. According to an XRD investigation, hydrogen insertion by spillover leads to a shortening of the *a*-axis (or contraction of the tunnel size) and an elongation of the *c*-axis; the formations of two distinct phases (I and II) were observed (Fig. 6). Similar changes in the axis lengths were also observed for samples highly hydrogenated by chemical reduction.[14] However, there was an apparent difference between the phase-change behaviors by spillover and a chemical reduction, as mentioned above. The sample prepared by spillover became a mixture of the two phases in the region $0.3 < x < 1.3$, while the one by chemical reduction became a single phase. Regarding the chemical composition, the two samples were different from each other. The former retained Na^+ ions in the tunnel sites, but had lost a large portion of its water species. On the other hand, the latter contained no Na^+ ion, but many water species (Fig. 5). The occupancy of the alkali metal cation in the tunnel site is seemingly related to the difference in the phase-change behavior. However, from an inspection of the relation between the phase and the compositional differences we suggest that the difference in the behavior is due to dehydration promoted by a non-wet condition during spillover. That is, the promoted dehydration during spillover leads to the formation of a largely distorted Mo–O framework (phase II) in samples even with low hydrogen contents, while the wet condition of the chemical reduction allows the sample to retain a larger water content, and to exhibit gradual structural changes.

New Synthesis Route for Alkali Metal Molybdenum Bronze. From investigating structural changes with heat-treatments in N_2 for hydrogenated samples, it was confirmed that alkali-metal molybdenum bronzes were obtained

Table 1. Crystallization Water and Dehydration Behavior

Host samples	Contents of water species in original samples [H_2O/Mo]				Slope[a] ($-\Delta H_2O/\Delta H$) of dehydration	Water content[a] after full hydrogenation [H_2O/Mo]
	Mo–CW	LW	OHW	A–CW		
Na	0.20	0.20	0.10	0.10	0.31	0.20
K	0.20	0.14	0.10	—	0.28	0.08
Cs	0.20	0.04	0.10	—	0.15	0.12

a) The values were obtained in situ.

at lower temperatures, ca. 200 K below the ordinary synthesis temperatures. However, hydrogenated samples, prepared from decamolybdates by spillover, exhibited an insufficient single-phase range (Fig. 6). We suppose that if the decamolybdates have no vacant Mo position, an enlarged single-phase range is expected for their hydrogenation compounds, because of no distortion due to dehydration. Fortunately, such a salt with an indefective tunnel structure has already been prepared.[31] We will make further investigations using the salt in the future.

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