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A Hydrogen Insertion Compound of Molybdenum Oxide Hydrate, $H_{0.12-0.22}MoO_3 \cdot H_2O$, and Its Formation Process from Hydrogen Molybdenum Bronze, H_xMoO_3

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Based on XRD and chemical analysis results, the hydrogen insertion compound of molybdenum oxide hydrate (H-hydrate) was suggested to be a genotypic compound of yellow molybdenum trioxide monohydrate, $MoO_3 \cdot H_2O$. H-hydrate was obtained in a hot HCl solution and in hot water from hydrogen molybdenum bronze, H_xMoO_3. The hydrogen bronze with $x \leqslant 0.24$ and the molybdenum species formed in the solution played a role in the formation of H-hydrate. In this process, a temporary dissolution of Mo^{5+} was observed at the beginning of the formation.

Many molybdenum oxide hydrates or a similar class of materials have been known.[1] In a previous study[2] we reported on the formation of a compound identical with or similar to $Mo_8O_{15}(OH)_{16}$[3,4] by treating a hydrogen molybdenum bronze, H_xMoO_3 ($0.23<x<0.40$), with aqueous HCl at 353 K. We regarded it as a hydrogen insertion compound of molybdenum oxide hydrate (H-hydrate), or a hydrate of a hydrogen insertion of molybdenum oxide, which could be expressed as $H_{0.15}MoO_3 \cdot 0.88H_2O$. However, we could not decide whether the compound was identical with $Mo_8O_{15}(OH)_{16}$ or not. $Mo_8O_{15}(OH)_{16}$ was discovered by Glemser and Lutz.[3] These authors obtained it by heating a mixture of yellow $MoO_3 \cdot 2H_2O$ and Mo without air at 383 K. In a series of studies they also obtained $Mo_4O_{10}(OH)_2$ and $Mo_2O_4(OH)_2$ by reducing MoO_3 with Zn/HCl or $SnCl_2$ and by heating a mixture of MoO_3, Mo, and H_2O without air at 383 K.[3] (Although these compounds are formulated as fixed compositions for convenience, they are nonstoichiometric compounds with a rather wide range of homogeneity.) With respect to $Mo_4O_{10}(OH)_2$ and $Mo_2O_4(OH)_2$, they introduced the concept of genotypic compounds of MoO_3, due to the close resemblance of their X-ray diffraction (XRD) patterns to that of the starting material (MoO_3). They also obtained other members, $Mo_5O_7(OH)_8$ and $Mo_5O_5(OH)_{10}$, and finally confirmed four phases of this series.[5,6] These four phases were studied in more detail by Birtill and Dickens.[7] They have been known as hydrogen insertion compounds of MoO_3, H_xMoO_3: 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 ($x=2.0$). On the other hand, $Mo_8O_{15}(OH)_{16}$ has been only reexamined by Rode and Lysanova[8] since Glemser and Lutz. According to TG-DTA and XRD results of yellow $MoO_3 \cdot 2H_2O$ by Sotani et al.,[9] the dihydrate decomposes to yellow monohydrate by releasing H_2O at the preparation temperature of $Mo_8O_{15}(OH)_{16}$ by Glemser and Lutz (383 K). This fact indicates that, though Glemser and Lutz used yellow dihydrate as a starting material, the true starting material of $Mo_8O_{15}(OH)_{16}$ was yellow monohydrate. (They believed that the hydration water of the dihydrate was completely released at 383 K and considered that the true starting material was MoO_3.) Moreover, Crouch-Baker and Dickens, recently, reported hydrogen insertion compounds of yellow hydrates of MoO_3, $H_1MoO_3 \cdot 2H_2O$ and $H_1MoO_3 \cdot H_2O$, obtained from yellow dihydrate and yellow monohydrate by catalytic hydrogenation (hydrogen spillover), and $H_xMoO_3 \cdot H_2O$ from $MoO_3 \cdot 2H_2O$ by reduction with acidified $SnCl_2$.[10] It is suggested that there is an intimate relation among the H-hydrates, $Mo_8O_{15}(OH)_{16}$, yellow monohydrate, $H_xMoO_3 \cdot H_2O$ and $H_1MoO_3 \cdot H_2O$; it is therefore important to discuss the relation.

In the present work, to obtain a single phase of H-hydrate, we explored its formation process, and succeeded in obtaining the single phase. The mechanism of H-hydrate formation was discussed. Based on XRD and chemical analysis results, the relation among H-hydrate, $Mo_8O_{15}(OH)_{16}$, $MoO_3 \cdot H_2O$, $H_xMoO_3 \cdot H_2O$ and $H_1MoO_3 \cdot H_2O$ was discussed briefly.

Experimental

Starting Materials. Three kinds of starting materials were used. The starting material with a maximum hydrogen content ($x=0.5$), called ST[1], was prepared by treating 30 g of MoO_3 with 6 g of Zn in 180 ml of a 2 M ($1 M=1 mol dm^{-3}$) HCl solution. ST[1] was a mixture of Type I and Type II hydrogen molybdenum bronzes by an XRD method. The starting material with a medium hydrogen content ($x=0.3$), called ST[2], was prepared by introducing 4 g of Zn. This was Type I. A starting material with a minimum hydrogen content ($x=0.15$), called ST[3], was prepared by introducing 2 g of Zn and was a mixture of Type I and MoO_3.

Investigation of H-Hydrate Formation Process and Characterization of the Specimens. The formation process of H-hydrate from the three starting materials at 343, 353, and 363 K was followed by investigating the specimens treated for a fixed time (1, 2, 4, 7, and 14 days long). Because Type I is soluble in alkaline solutions, we chose three kinds of treating solutions: a 1 M HCl acid solution (non oxidative), a 1 M

HNO_3 acid solution (oxidative) and distilled water. Then, 3 g of the starting material was treated by 150 ml of each treating solution. After treatment the specimens were cooled to room temperature, filtrated, washed with water and vacuum-dried for one day. They were then investigated by using an XRD method and by chemical analysis. The XRD measurement was carried out using a Rigakudenki RINT 1200M diffractometer with Cu K_α radiation. The x values (i.e., hydrogen content) of the specimens were determined by Choain and Marion's method.[11] According to XRD results, most of the specimens were a mixture of the starting materials and/or H-hydrate. Because Type I, Type II, and H-hydrate completely turned to MoO_3 at 673 K in air, the x value was evaluated from the specimen weight at 673 K (Thermogravimetry). Molybdenum species dissolved in the treating solutions from the specimens were investigated by UV-visible spectroscopy.

With respect to 1 M HNO_3 treatments, all specimens were oxidized to MoO_3.

Results and Discussion

H-Hydrate. In this study, we obtained many resulting specimens which did not contain MoO_3 or H_xMoO_3. These specimens showed the XRD peaks of H-hydrate described in our previous study,[2] and were referred to as H-hydrate specimens. They were blue in color and had the composition $H_{0.14-0.22}MoO_3 \cdot 0.94—1.04H_2O$. The specimens did not release hydration water below 373 K and their compositions did not change upon a further vacuum drying. Upon standing in an air atmosphere for a long time, the x value gradually decreased; for example by standing for one year the specimens with $H_{0.21}$ and $H_{0.14}$ turned to those with $H_{0.16}$ and $H_{0.12}$, respectively. The XRD patterns of several freshly prepared specimens are shown in Fig. 1. These patterns are similar to each other, except for the pattern of the specimen with x=0.14. There are minor differences concerning the peaks at 16.9, 25.0, and 33.1°, which disappear when the peaks at 22.9 and 23.5° become broad. An inspection of Fig. 1 is likely to indicate that the disappearance of the peaks depends on the x value, but there was no change in their XRD patterns with a decrease in the x value upon standing in an air atmosphere.

The specimens show almost the same XRD pattern, although they were prepared under various conditions and their compositions cover a rather wide range ($H_{0.12-0.22}MoO_3 \cdot y$ H_2O, y=about 1). The disappearance of the XRD peaks at 16.9, 25.0, and 33.1° does not depend on the x values and water content of the specimens, but are accompanied by a broadening of the peaks at 22.9 and 23.5°. We presume that the disappearance is related to distortion in the crystal lattice of the specimens. The x values in Fig. 1 can be regarded as being those during the formation of H-hydrate. The seeming dependence of the XRD pattern on the x value, which is observed in Fig. 1, may indicate that the x value during the formation affects the distortion. According to the Raman results,[12] there were no significant differences between the specimens with x=0.21 and x=0.14 in Fig. 1. Therefore, we believe that all H-hydrate specimens are of the same species; that is, they consist of a single phase of a nonstoichiometric compound with a rather wide range of homogeneity. We suggest that the XRD pattern with peaks at 16.9, 25.0, and 33.1° is typical of H-hydrate. Accurate d-spacings are shown in Table 1. Although we have tried to index them using an indexing program for powder XRD pattern,[13]

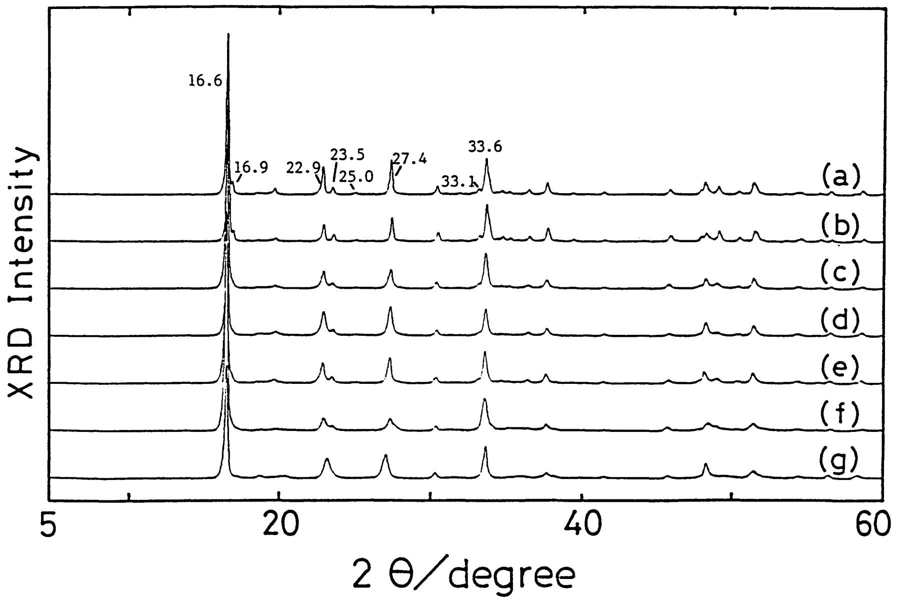

Fig. 1. Powder XRD patterns of the specimens; (a) $H_{0.22}MoO_3 \cdot 0.97H_2O$, (b) $H_{0.21}MoO_3 \cdot 1.01H_2O$, (c) $H_{0.20}MoO_3 \cdot 1.02H_2O$, (d) $H_{0.19}MoO_3 \cdot 1.02H_2O$, (e) $H_{0.18}MoO_3 \cdot 1.03H_2O$, (f) $H_{0.17}MoO_3 \cdot 1.01H_2O$, and (g) $H_{0.14}MoO_3 \cdot 0.99H_2O$.

we have not yet obtained suitable results, because the XRD pattern is too complicated.

Figure 2 shows a comparison among the XRD patterns of H-hydrate, $Mo_8O_{15}(OH)_{16}$,[3] yellow $MoO_3 \cdot H_2O$ (JCPDS 28-0666), $H_xMoO_3 \cdot H_2O$ (JCPDS 38-0066) and $H_1MoO_3 \cdot H_2O$ (JCPDS 38-0064). The XRD pattern of H-hydrate is similar to that of $Mo_8O_{15}(OH)_{16}$, except for several small peaks. According to Glemser and Lutz,[3] $Mo_8O_{15}(OH)_{16}$ was also expressed by the composition $MoO_{2.88-2.90} \cdot H_2O$. Because the composition of H-hydrate can be rewritten as $MoO_{2.89-2.94} \cdot 1.04—1.16H_2O$, H-hydrate and $Mo_8O_{15}(OH)_{16}$ are comparable to each other. On the basis of their XRD patterns and compositions, H-hydrate is identical with $Mo_8O_{15}(OH)_{16}$. The XRD pattern of $MoO_3 \cdot H_2O$ shows two strong diffraction peaks at about 16.5 and 33.0°, which are attributed to the (020) and (040) planes. This hydrate has a layer structure, and the *d*-spacing of

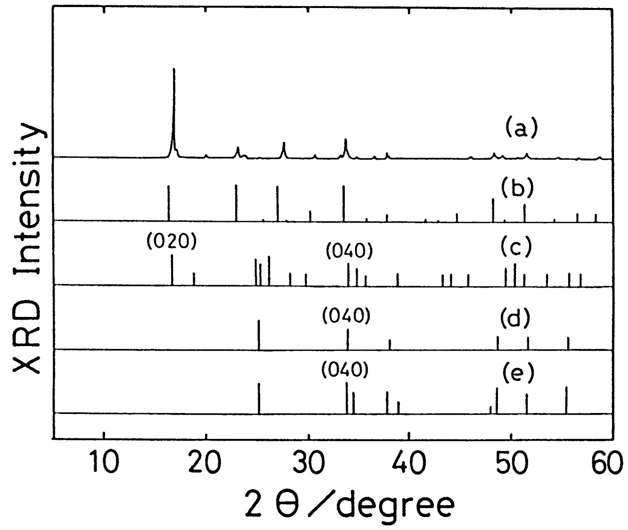

Fig. 2. Powder XRD patterns of H-hydrate (a), $Mo_8O_{15}(OH)_{16}$ (b), yellow $MoO_3 \cdot H_2O$ (c), $H_xMoO_3 \cdot H_2O$ (d), and $H_1MoO_3 \cdot H_2O$ (e).

Table 1. *d*-Spacings of H-Hydrate

2θ	d	I/I_1	2θ	d	I/I_1
16.590	5.339	100	35.104	2.554	2
16.900	5.242	8	36.436	2.464	2
17.880	4.957	1	37.672	2.386	5
18.578	4.772	1	39.360	2.287	1
19.374	4.578	1	41.468	2.1758	1
19.742	4.493	2	45.874	1.9765	2
22.896	3.881	6	47.884	1.8981	2
23.530	3.778	3	48.232	1.8852	3
25.016	3.557	1	49.028	1.8565	4
27.376	3.255	7	50.400	1.8091	2
30.382	2.940	3	51.380	1.7769	5
30.928	2.889	1	51.844	1.7621	1
31.846	2.808	1	53.300	1.7173	1
33.106	2.704	3	54.352	1.6865	2
33.580	2.667	19	55.636	1.6506	1
33.738	2.654	9	56.428	1.6293	1
34.260	2.615	2	57.946	1.5902	1
34.640	2.587	2	58.834	1.5756	2

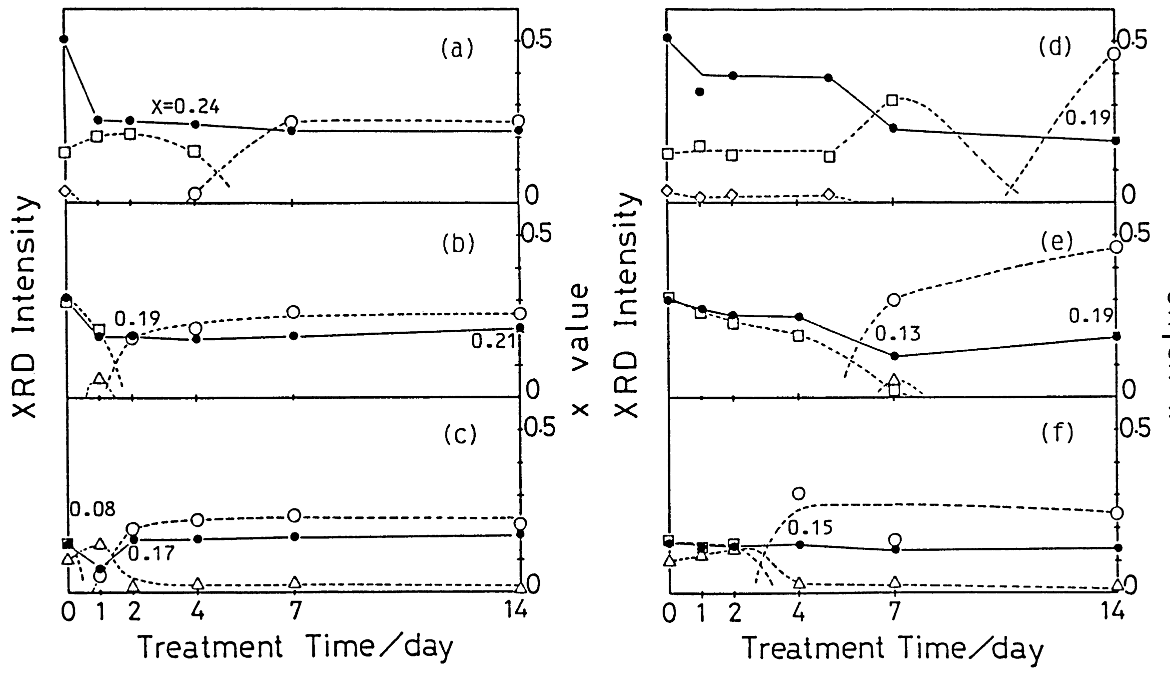

Fig. 3. Formation process of H-hydrate at 353 K by the HCl treatment from ST[1] (a), ST[2] (b), and ST[3] (c), and by the water treatment from ST[1] (d), ST[2] (e), and ST[3] (f), respectively. (□), (◇), (△), and (○) are the relative XRD intensity of the peak at 25.3° of Type I to the intensity of the peak at 28.4° of Si which was mixed with the specimens as an internal standard, that of the peak at 24.2° of Type II, that of the peak at 25.7° of MoO_3 and that of the peak at 16.6° of H-Hydrate, respectively. (●) is the x value of the specimen.

the (020) plane corresponds to its interlayer spacing. The XRD patterns of $H_xMoO_3 \cdot H_2O$ and $H_1MoO_3 \cdot H_2O$ also show a strong peak at about 33.0°, which is ascribed to the (040) plane. This indicates that $H_xMoO_3 \cdot H_2O$ and $H_1MoO_3 \cdot H_2O$ retain the Mo–O framework of $MoO_3 \cdot H_2O$. The two strong peaks are observed in the patterns of H-hydrate and $Mo_8O_{15}(OH)_{16}$. This fact indicates a resemblance in Mo–O framework among H-hydrate, $Mo_8O_{15}(OH)_{16}$, and yellow monohydrate. Because the starting material of $Mo_8O_{15}(OH)_{16}$ is yellow monohydrate, we suggest that $Mo_8O_{15}(OH)_{16}$, i.e., H-hydrate, is a genotypic compound of yellow monohydrate. We, thus, express H-hydrate as $H_{0.12-0.22}MoO_3 \cdot H_2O$.

The Formation Process. Figure 3 shows the formation process of H-hydrate from the three starting materials at 353 K. In the case of an HCl treatment, H-hydrate appears after 4 days of treatment for ST[1], 2 days for ST[2], and 1 day for ST[3]. In the case of a water treatment, H-hydrate formation is also observed. There is basically no difference between the results for an HCl treatment and that for a water treatment, except that H-hydrate is formed much more slowly in water than in an HCl solution. The formation of H-hydrate took place little more rapidly at 363 K, and slightly more slowly at 343 K than at 353 K. In several cases, MoO_3 temporarily appeared, or temporarily increased, just before H-hydrate appeared. This appearance or increase of MoO_3 was accompanied by a decrease in the x value. In the case of an HCl treatment at 353 K for ST[1], H-hydrate was formed without the appearance of MoO_3. In all cases, H-hydrate was formed as Type I disappeared. The formation took place when the x value of the solid phase was in the range $x \leqslant 0.24$ and Type II was not contained.

The formation of H-hydrate, followed by the disappearance of Type I, indicates that H-hydrate is formed from Type I. The maximum limit value ($x=0.24$) corresponds to the reduction degree [$MoO_{2.88}$]. This reduction degree is identical with that of $Mo_8O_{15}(OH)_{16}$,[3] i.e., that of H-hydrate. The temporary appearance, or temporary increase, of MoO_3 seems to be correlated with the formation of H-hydrate. However, as mentioned above, in the case of an HCl treatment of ST[1] at 353 K, formation took place without the appearance of MoO_3. To investigate whether the appearance or increase of MoO_3 is correlated with the formation, we paid much attention to specimens which contained both H-hydrate and Type I, i.e., which revealed a H-hydrate forming stage. It was then recognized that the specimens at this stage contained MoO_3 when $x<0.23$. Therefore, the appearance, or increase, of MoO_3 is not correlated with the formation of H-hydrate. It has been known that H_xMoO_3 in the range $x<0.23$ exists as a mixture of Type I and MoO_3.[7] As mentioned above, a temporary decrease in the x value was also observed just before H-hydrate formation. The temporary appearance, or temporary increase, of MoO_3 arises from a temporary decrease in the x value to less than 0.23. The temporary decrease in the x value indicates that Mo^{5+} was temporarily dissolved into the treating solution. We presume that this dissolution of Mo^{5+} takes place when the Mo–O framework based on the MoO_3 structure (H_xMoO_3) is reformed to that based on the $MoO_3 \cdot H_2O$ structure (H-hydrate).

For an HCl treatment, the supernatant solution was orange in color before H-hydrate formation took place; the color became faint as the formation proceeded. For water treatment, however, the supernatant was deep dark blue before formation, and finally the color turned to faint greenish blue. Figure 4 shows the UV-visible spectra of the supernatant solutions for ST[3]. Spectra (a) and (b) were obtained from orange (for 1 day HCl treatment at 353 K) and colorless (for 4 days HCl treatment at 353 K) supernatant solutions, respectively, while spectra (c) and (d) were obtained from deep dark blue (for 1 day water treatment at 353 K) and faint greenish blue (for 4 days water treatment at 353 K) solutions, respectively. Spectrum (a) shows a strong band below 350 nm and two weak bands at 380 and 480 nm. Spectrum (c) shows a strong band below 350 nm

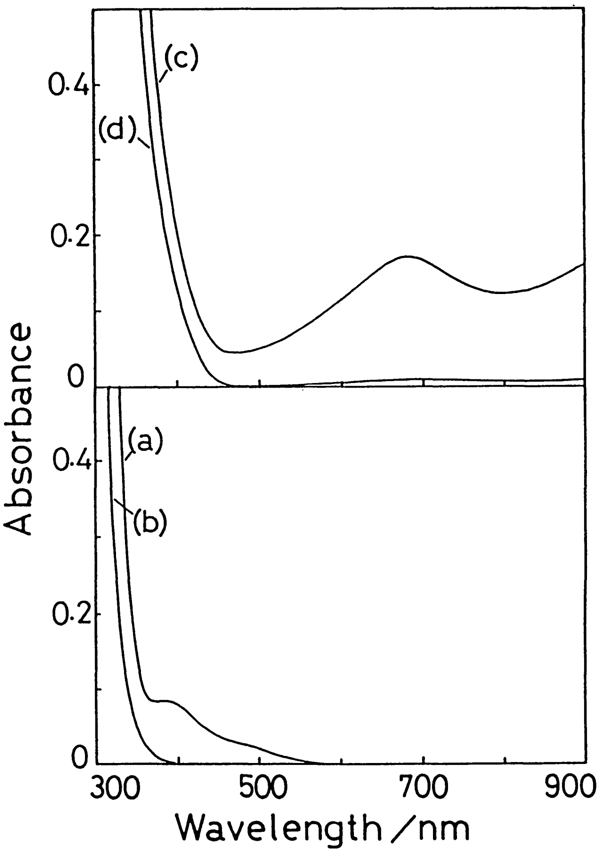

Fig. 4. Extinction spectra of supernatant solutions for HCl and water treatments of ST[3] at 353 K. The (a) and (b) spectra were obtained from the solutions for 1 day and 4 days HCl treatments, respectively, while (c) and (d), for 1 day and 4 days water treatments, respectively.

and two medium bands at 680 nm and above 900 nm. These observed bands arise from molybdenum species dissolved in the treating solutions from H_xMoO_3. The strong band below 350 nm, observed in both spectra (a) and (c), is attributed to molybdenum species consisting of Mo^{6+}. The bands at 380 and 480 nm are ascribed to mixed-valence (Mo^{6+} and Mo^{5+}) molybdenum species with a small degree of condensation, such as a dimer,[14] while the bands at 680 nm and above 900 nm are ascribed to mixed-valence molybdenum species with a large degree of condensation, which are known as isopoly-blue. The following information can be obtained from Fig. 4: (i) As the formation of H-hydrate proceeds, the amount of mixed-valence species apparently decreases. (ii) The forms of mixed-valence species depend on the treating solution; no mixed-valence molybdenum species common to both treating solutions has been observed.

This information suggests that the mixed-valence molybdenum species in the treating solution plays a role in the formation of H-hydrate. However, H-hydrate is not formed only by condensation of the molybdenum species in solution. If H-hydrate is formed only by condensation, any common mixed-valence molybdenum species with an extremely large degree of condensation should be observed in both HCl and water treating solutions during formation. As mentioned above, H-hydrate formation also depended on the x value of the solid phase (When $x \leqslant 0.24$, the formation of H-hydrate was observed). Thus, both the (mixed-valence) molybdenum species in the treating solution and H_xMoO_3, $x \leqslant 0.24$ correlate strongly with the formation of H-hydrate. There is still a question as to why these different species in an HCl solution and in water lead to the same product (H-hydrate). This question can be answered by considering that these species may also comprise of the same constituent unit, i.e., Mo–O octahedra, as H-hydrate (monohydrate of MoO_3), MoO_3, and H_xMoO_3. Mo^{5+} seems to be necessary for molybdenum species to react with the solid phase and to form H-hydrate. We conclude that H-hydrate is formed as follows:

$$\begin{tikzcd}
\text{Molybdenum species} & \text{Molybdenum species (mixed-valence)} \arrow[d, "+H_2O"] & \\
H_xMoO_3 \arrow[u, "\text{dissolution}"] \arrow[r] & \begin{array}{c} H_xMoO_3 \\ \text{[Solid phase]} \\ x \leqslant 0.24 \end{array} \arrow[r] & \text{H-hydrate}
\end{tikzcd}$$

References

1) "Gmelin Handbook, Mo," Vol. B3a, 1987.

2) K. Eda and N. Sotani, *Bull. Chem. Soc. Jpn.,* **62**, 4039 (1989).

3) O. Glemser and G. Lutz, *Z. Anorg. Allg. Chem.,* **264**, 17 (1951).

4) O. Glemser, *Nachr. Akad. Wiss. Göttingen, Math. Phys.,* **1955**, 121.

5) O. Glemser, U. Hauschild, and G. Lutz, *Z. Anorg. Allg. Chem.,* **269**, 93 (1952).

6) O. Glemser, G. Lutz, and G. Meyer, *Z. Anorg. Allg. Chem.,* **285**, 173 (1956).

7) J. J Birtill and P. G. Dickens, *Mater. Res. Bull.,* **13**, 311 (1978).

8) E. Ya. Rode and G. V. Lysanova, *Dokl. Akad. Nauk SSSR,* **145**, 573 (1962).

9) N. Sotani, Y. Saito, M. Oita, and M. Hasegawa, *Nippon Kagaku Kaishi,* **1974**, 673.

10) S. Crouch-Baker and P.G. Dickens, *Mater. Res. Bull.,* **19**, 1457 (1984).

11) C. Choain and F. Marion, *Bull. Soc. Chim. Fr.,* **1963**, 212.

12) The specimens showed the same bands at 200, 260, 375, 640, 805, 890, 930, and 940 cm^{-1}. Degradation by laser irradiation did not take place.

13) J. W. Visser, *J. Appl. Crystallogr.,* **2**, 89 (1969), and references therein.

14) M. T. Pope, "Heteropoly and Isopoly Oxometalates," Springer-Verlag, Berlin, Heidelberg, New York, Tokyo (1983), Chap. 3, p. 48.