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Calorimetric study of hydrated sodium molybdenum bronze

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Abstract

Several kinds of hydrated sodium bronze with various amount of hydrogens were synthesized and the standard enthalpies of formation were determined by solution calorimetry. These enthalpies were summarized by least square method and were compared with the enthalpies of formation of hydrogen bronzes. It was found that the enthalpy of formation of the hydrated sodium bronzes was smaller than that of the hydrogen bronze and decreased with the increase in hydrogen content.

Keywords: X-ray diffractometer; Hydration energy; Entropy

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1. Introduction

It is well-known that the structure of alkali decamolybdates has a hexagonal crystal structure, which consists of double chains of edge and corner sharing MoO_6 octahedra with hexagonal channels (tunnel); see description in the references [1–3]. The inserted alkali ions closely relate to the framework of the crystal structure. Investigation of the thermodynamic behavior of insertion of alkali ions into tunnel space is very important to discuss thermodynamically on the stability of framework structure and the property of alkali decamolybdate. In the previous report [4], the authors determined the standard enthalpy of formation of alkali decamolybdates with tunnel structure. We discussed the relation between the thermodynamic quantities and the crystal structure depended on the size of inserted alkali ions [4], and revealed that the inserted cations affected the crystal structure and the standard enthalpy of formation of alkali decamolybdates with the constant valence number of Mo^{6+}. However, the influence of valence number of molybdenum has not been considered, because in the case of typical mixed valence compounds, such as the hydrated alkali molybdenum bronzes, the valence number is affected largely, though the structure is not affected largely. Therefore, the relation between the enthalpy and the valence number of Mo atom is very interesting to be studied. The hydrated sodium molybdenum bronze has the layer structure, in which the sodium metal ion with two hydrate waters for one sodium ion is inserted [5]. The hydrated sodium molybdenum bronze has the six-coordination structure, as shown in Fig. 1b. When the excess reduction of molybdenum atom takes place, in addition to the sodium ions, the hydrogens are inserted to compensate the charge balance to form hydrogen co-inserted hydrated sodium molybdenum bronze. Hydrogen molybdenum bronzes have four phases with different valence of Mo. Birtill and Dickens [6] determined

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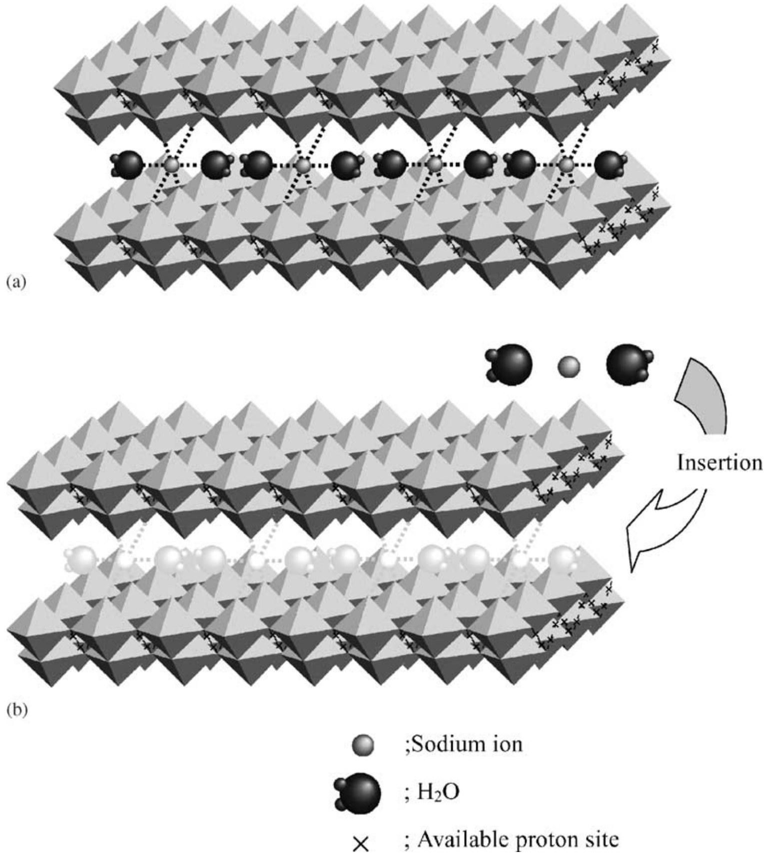

Fig. 1. (a) Insertion model of hydrated sodium ion $(Na{\cdot}2H_2O)^+$ into MoO_3 sheets and (b) the crystal structure of hydrated sodium bronze.

the standard molar enthalpy of formation of hydrogen molybdenum bronzes ($0 < x \leqq 2$) and discussed the relation between the thermodynamic function and the valence number of molybdenum. Considering their results, it is expected that the valence number of molybdenum of hydrated molybdenum bronze may relate to their thermodynamic functions and the stability of the structure.

In this paper, in order to confirm the relation between the valence number of molybdenum atoms and the standard enthalpy of formation, $\Delta_f H^\circ$, we determined $\Delta_f H^\circ$ of several kinds of hydrogen co-inserted hydrated sodium molybdenum bronze, $Na_{0.25}H_xMoO_3{\cdot}0.50H_2O$, with various reduction state, and discussed their relation and the valence number and the stability of hydrated molybdenum bronze with the different valence.

2. Experimental

2.1. Materials

Hydrogen co-inserted hydrated sodium molybdenum bronzes, $Na_{0.25}H_xMoO_3{\cdot}0.50H_2O$, with various reduction state were obtained. Twenty grams of MoO_3 (Wako pure chemical industries, Ltd.) was suspended in 200 ml distilled water at 276–278 K, which was stirred with a magnetic stirrer. Eight grams of $Na_2S_2O_4$ (Wako pure chemical industries, Ltd.) and 60 g of $Na_2MoO_4{\cdot}2H_2O$ (buffer agent, Wako pure chemical industries, Ltd.) were mixed well, which was added by the several times, and then stirred for 1 day. The sample was collected by suction filtration, washed well with distilled water, and vacuum-dried. The samples were confirmed to be a single pure phase by X-ray diffraction. The samples are very stable in nitrogen atmosphere, but in air or under the vacuum they release hydrogens very slowly. Therefore, we can control hydrogen content by leaving the sample in air atmosphere or by electromicro balance under the caluum.

2.2. Structure and chemical composition

The water contents of the samples were determined by TG-DTA on a Mac Science TG-DTA 2010S system from room temperature to 773 K at a heating rate of 10 K min^{-1} in nitrogen and by gravimetry on a Cahn 2000 electro microbalance from room temperature to 773 K at a heating rate of 10 K min^{-1} under the vacuum. The sodium and molybdenum contents were measured with a Hitachi 180–80 atomic absorption spectrometer using the 589.00 nm line for sodium and the 313.26 nm line for molybdenum. X-ray diffraction (XRD) patterns of the samples were obtained using a Mac Science XMP3 X-ray diffractometer with Cu Kα radiation. The content of Mo^{5+} was determined by using the method of Choain and Marrion [7].

The compositions of the hydrogen co-inserted hydrated sodium molybdenum bronzes were $Na_{0.25}H_x MoO_3{\cdot}0.50H_2O$ ($0 \leqq x \leqq 0.19$).

2.3. Calorimetric procedure

The heat of dissolution of the sample was measured by means of a Tokyo-Riko MMC-5111 multi-microcalorimeter (conduction type twin calorimeter). The heat flux due to the dissolution of the sample was converted to a potential and was recorded by a personal computer at a sampling interval of 1 s. The heats were estimated from the peak area appearing on the heat flux curve by comparison with that due to Joule heat. The internal temperature of the calorimeter was adjusted precisely at 298.15 ± 0.001 K and was monitored using a Beckmann's thermometer calibrated with a $A\Sigma\Lambda$ F-25 precision platinum resistance thermometer. The precision of the calorimeter was reported previously [4,8].

Hydrated sodium bronze with various valence sealed in a glass ampoule was set in the calorimeter with 30 ml batches of calorimetric reaction medium, which was prepared by dissolving 40 g of $K_3Fe(CN)_6$ in 1990 ml of 3.00 M KOH aqueous solution [5]. The standard molar enthalpies of formation of hydrated sodium bronzes with various valence were estimated from the observed dissolution heats by Hess's law of heat summation.

3. Results and discussion

The calorimetric reaction schemes used for the determination of the enthalpy of formation of $Na_{0.25}H_xMoO_3{\cdot}0.50H_2O$ are given in Table 1 together with the average measured heats of reaction for five times and their uncertainties. The standard enthalpy of formation of $Na_{0.25}H_xMoO_3{\cdot}0.50H_2O$, $\Delta_f H^\circ(x)$ can be estimated as following Eq. (1);

$$\begin{aligned} &Na_{0.25}H_xMoO_3 \cdot 0.50H_2O(s) + 0.25HCl(l) \\ &\quad = \frac{x+0.25}{2} MoO_2(s) + \frac{1.75-x}{2} MoO_3(s) \\ &\qquad + 0.25NaCl(s) + \left(0.50 + \frac{x+0.25}{2}\right) H_2O(l). \end{aligned} \tag{1}$$

From Eq. (1), $\Delta_f H^\circ(x)$ is determined to be

$$\begin{aligned} &\Delta_f H^\circ(Na_{0.25}H_xMoO_3 \cdot 0.50H_2O) \\ &\quad = \frac{x+0.25}{2} \Delta_f H^\circ(MoO_2) + \frac{1.75-x}{2} \Delta_f H^\circ(MoO_3) \\ &\qquad + 0.25\,\Delta_f H^\circ(NaCl) + \left\{0.50 + \frac{x+0.25}{2}\right\} \\ &\qquad \times \Delta_f H^\circ(H_2O) - x\,\Delta_f H^\circ(HCl) - \Delta H_0(x), \end{aligned}$$

where $\Delta H_0(x)$ is the heat of reaction (1) with hydrogen content x. $\Delta H_0(x)$ is obtained from the data (ΔH_2–ΔH_6) in Table 1. Once we obtain $\Delta H_0(x)$, $\Delta_f H^\circ(Na_{0.25}H_xMoO_3{\cdot}0.50H_2O)$ is easily determined. The standard enthalpies of formation, $\Delta_f H^\circ$, for each compounds are already confirmed as listed in Table 2. Using these data, the standard enthalpies of formation of hydrated sodium bronze with various reduction state (298.15 K) were determined using

$$\Delta_f H^\circ = A(x) - \Delta H_0(x),$$

Table 1
Calorimetric reaction scheme for $Na_{0.25}H_xMoO_3 \cdot 0.50H_2O$

Reaction	ΔH°/kJ mol^{-1}[a]
(1) $Na_{0.25}H_xMoO_3 \cdot 0.50H_2O(s) + (0.25 + x)Fe(CN)_6^{3-}(solution) + (2 + x)OH^-(solution)$ $= 0.25Na^+(solution) + MoO_4^{2-}(solution) + (0.25 + x)Fe(CN)_6^{4-} + (1 + x + 0.50)H_2O(solution)$	ΔH_1
(2) $MoO_2(s) + 2Fe(CN)_6^{3-}(solution) + 4OH^-(solution)$ $= MoO_4^{2-}(solution) + 2Fe(CN)_6^{4-}(solution) + 2H_2O(solution)$	$\Delta H_2 = -293.62 \pm 0.58$
(3) $MoO_3(s) + 2OH^-(solution) = MoO_4^{2-}(solution) + H_2O(solution)$	$\Delta H_3 = -85.20 \pm 0.18$
(4) $NaCl(s) = Na^+(solution) + Cl^-(solution)$	$\Delta H_4 = -0.4193 \pm 0.0401$
(5) $HCl(l) + OH^-(solution) = H_2O(solution) + Cl^-(solution)$	$\Delta H_5 = -65.85 \pm 0.52$
(6) $H_2O(l) = H_2O(solution)$	$\Delta H_6 = -0.061 \pm 0.003$
(0) $Na_{0.25}H_xMoO_3 \cdot 0.50H_2O(s) + 0.25HCl(l)$ $= (x + 0.25)/2MoO_2(s) + (2 - 0.25 - x)/2MoO_3(s) + 0.25NaCl(s)$ $+\{0.50+(x+0.25)/2\}H_2O(l)\ \Delta H_0(x)$ $\Delta H_0(x) = \Delta H_1 - (0.25+x)/2\Delta H_2 - (2 - 0.25 - x)/2\Delta H_3 - 0.25\Delta H_4 + 0.25\Delta H_5$ $-\{0.50 + (0.25 + x)/2\}\Delta H_6$	

[a] Uncertainties expressed as twice the standard error of the mean.

where

$$\begin{aligned} A(x) = {} & \frac{x + 0.25}{2}\Delta_f H^0(MoO_2) \\ & + \frac{1.75 - x}{2}\Delta_f H^0(MoO_3) \\ & + 0.25\Delta_f H^\circ(NaCl) \\ & + \left(0.50 + \frac{x + 0.25}{2}\right)\Delta_f H^\circ(H_2O) \\ & - x\,\Delta_f H^\circ(HCl). \end{aligned}$$

3.1. Standard enthalpy of formation of hydrated sodium molybdenum bronze with various reduction state

Changes in $\Delta_f H^\circ$ of hydrated sodium bronze and of hydrogen bronze against the hydrogen content, x, are shown in Fig. 2. $\Delta_f H^\circ$ decreases with the increment of hydrogen contents. At $x = 0$, the standard enthalpy of formation of hydrated sodium bronze (-961.1 kJ mol^{-1}) is smaller than that of MoO_3 (-745.2 kJ mol^{-1}). This enthalpy gap (215.9 kJ mol^{-1}) depends on the standard enthalpy of formation of ($Na^+ \cdot 2H_2O$) ions and the insertion enthalpy of hydrated sodium ion to MoO_3 sheets as shown in Eq. (2).

Table 2
Standard molar enthalpies used to determine the standard molar enthalpies of formation of the hydrated sodium bronzes[a]

	$\Delta_f H^\circ$ (kJ mol^{-1})
MoO_3	−745.2
MoO_2	−587.9
HCl (0.10 M)	−165.47
H_2O	−285.830
NaCl	−411.1

[a] See Chapter 8, p. 953 [9].

$$MoO_3(s) + 0.25\{Na^+ \cdot 2H_2O(l)\} \overset{\Delta_{insert}H_2^\circ}{=} (Na \cdot 2H_2O)0.25MoO_3(s) \qquad (2)$$

Estimation of hydration energy of Na^+ is very difficult. Generally, the number of hydration of Na^+ in

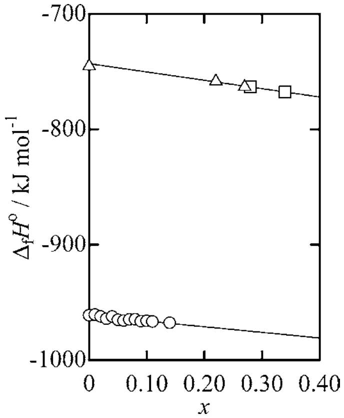

Fig. 2. Standard enthalpies of formation. (○): $(Na \cdot 2H_2O)_{0.25}H_xMoO_3$ of this work; (□) and (△): H_xMoO_3 of Birtill and Dickens [6] and Suzuki et al. [4], respectively.

aqueous solution had been measured by many methods. In the case of Na^+, it is well-known that Na^+ is surrounded with six water molecules [8]. It is supported by XRD and EXAFS [9] results. The hydration waters in hydrated bronze is two per one Mo atom, as described earlier. The hydration energy surrounded with six water molecules is $-403.8\,kJ\,mol^{-1}$ [10]. So, the hydration energy of Na^+ with two hydrate waters can be simply estimated to divide by 3 to be

$$\frac{-403.8\,kJ\,mol^{-1}}{3} = -134.6\,kJ\,mol^{-1}$$

Accordingly, $\Delta_{insert}H_2^\circ$ is estimated to be

$$\begin{aligned}\Delta_{insert}H_2^\circ &= \Delta_f H^\circ\{(Na\cdot 2H_2O)_{0.25}MoO_3(s)\}\\ &\quad -\Delta_f H^\circ\{(MoO_3)(s)\}\\ &\quad -0.25\,\Delta_f H^\circ\{Na+(2H_2O)(s)\}\\ &= -961.1\,kJ\,mol^{-1} - (-745.2\,kJ\,mol^{-1})\\ &\quad -0.25(-134.6\,kJ\,mol^{-1}) = -182.2\,kJ\,mol^{-1}.\end{aligned}$$

It is shown that $\Delta_{insert}H^\circ{}_2$ ($-182.2\,kJ\,mol^{-1}$) is very close to the difference ($-215.9\,kJ\,mol^{-1}$) between $\Delta_f H^\circ\{(MoO_3)(s)\}$ and $\Delta_f H^\circ\{(Na\cdot 2H_2O)_{0.25}MoO_3(s)\}$. The heat of insertion is relatively large. As mentioned earlier, hydrated Na^+ ion has each one water molecule at both sides. The interaction between the hydrogen atoms of hydration water molecule and the terminal oxygen atoms of the MoO_6 octahedra constructed the MoO_3 sheets should take place and their influence should contribute greatly to the heat of insertion. On the other hand, we reported [11] that the change in oxidation state (reduction degree) effected the heat of formation of molybdenum oxide. By insertion of hydrated Na^+ and H^+ ions into MoO_3 sheets, Na^+ and H^+ compensate the charge within the compound. The part of reduced Mo depends on the concentration of Na^+ and H^+ controlled by the preparation conditions as shown in Fig. 1a.

Generally, hydrated sodium bronze contains a small amount of hydrogen, x, and is presented as $(Na\cdot 2H_2O)_yH_xMoO_3$. Therefore, the valence number of Mo may change by changing both x and y. However, in this work, $\Delta_f H$ of hydrated sodium bronze depends on only hydrogen content because the sodium ion content is fixed constant to be 0.25. Fig. 2 shows the $\Delta_f H^\circ(x)$ of hydrated sodium bronze and hydrogen bronze, which decrease with the increment of hydrogen content, x. Therefore, it is suggested that the change in $\Delta_f H^\circ$ of hydrated sodium bronze and hydrogen bronze depends on the effect of the insertion of hydrogen. Also the change in $\Delta_f H^\circ$ of hydrogen bronze is shown in Fig. 2. The slope of $-\Delta_f H^\circ(x)$ of hydrated sodium bronze and hydrogen bronze is 48.5 and $65.5\,kJ\,mol^{-1}$, respectively. Considering that the effect of hydrogen insertion, the slope of hydrated bronze and hydrogen bronze should be the same. However, the slope of hydrated bronze is smaller than that of hydrogen bronze. This suggests that the effect of hydrogen insertion is different between in hydrogen bronze and in hydrated sodium bronze. This means that the effect of hydrogen insertion is weakened by the presence of hydrated sodium ions. That is, by the insertion of hydrogen, the interaction between hydrogen and hydrated sodium ions take place. The standard enthalpy of formation of $(Na\cdot 2H_2O)_{0.23}MoO_3$ was also determined by solution calorimetry to be $-941.9\,kJ\,mol^{-1}$. This value was higher by $19.2\,kJ\,mol^{-1}$ than $\Delta_f H^\circ$ of $(Na\cdot 2H_2O)_{0.25}MoO_3$. The further insertion process is estimated using Eq. (3).

$$(Na\cdot 2H_2O)_{0.23}MoO_3(s) + 0.02\{Na^+\cdot 2H_2O(l)\} \overset{\Delta_{insert}H_3^\circ}{=} (Na\cdot 2H_2O)_{0.25}MoO_3(s) \quad (3)$$

$\Delta_f H$ of $(Na^+\cdot 2H_2O)_{0.02}$ is estimated to be 0.02 $(-134.6\ kJ\,mol^{-1}) = -2.7\,kJ\,mol^{-1}$, where $\Delta_f H$ of $(Na\cdot 2H_2O)_{0.25}$ is $-134.6\,kJ\,mol^{-1}$. The enthalpy of insertion, $\Delta_{insert}H^\circ$, in Eq. (3) is estimated simply to be

$$\begin{aligned}\Delta_{insert}H_3^\circ &= \Delta_f H^\circ\{(Na\cdot 2H_2O)_{0.25}MoO_3(s)\}\\ &\quad - \Delta_f H^\circ\{(Na\cdot 2H_2O)_{0.23}MoO_3(s)\}\\ &\quad - 0.02\,\Delta_f H^\circ\{Na+(2H_2O)(s)\}\\ &= -961.1\,kJ\,mol^{-1} - (-941.9\,kJ\,mol^{-1})\\ &\quad - 0.02\times(-134.6\,kJ\,mol^{-1})\\ &= -16.5\,kJ\,mol^{-1}. \end{aligned} \quad (4)$$

The further insertion of hydrated sodium ions into $(Na\cdot 2H_2O)_{0.23}MoO_3$ to form $(Na\cdot 2H_2O)_{0.25}MoO_3$ proceeds rather easily, according to our experiment. Results of Eq. (4) shows that $\Delta_{insert}H^\circ$ is negative. Considering that the change in the entropy of insertion, $\Delta_{insert}S^\circ$, is very small, $\Delta_{insert}G^\circ$ is negative. Therefore, this supports that the Eq. (3) takes place easily.

4. Conclusion

The standard enthalpies of formation of hydrated sodium bronzes were determined by Hess's law of the heat summation. The standard enthalpy of formation of sodium bronze depends on hydrogen insertion, which is affected by the interaction between inserted hydrogens and hydrated sodium ions. This results is expected to apply for design of new functional compounds.

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