Formation and Thermal Behavior of Metal Hydroxide-Intercalated Tantalum Disulfide

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Formation and thermal behavior of metal hydroxide intercalated tantalum disulfide were studied. Intercalation of hydroxides into β -TaS₂ resulted in the expansion of layer spacing by 5.8 Å (type I) or by 2.9 Å (type II), the intercalation of NaOH and Ca(OH)₂ gave the former type, while that of LiOH, KOH and Ba(OH)₂ gave the latter. It was found that the expansion was controlled by the amounts of water incorporated together with the guest hydroxides. On dehydration by evacuation or heating, the layer spacing became narrower consecutively to form three new types, III, IV and V, the layer spacings of which were larger by 1.5, 0.8 and 0.3 Å than that in β -TaS₂, respectively. It was deduced that all these five types were related with each other in a characteristic manner which was best accounted for by assuming stage compounds.

1 Introduction

Tantalum disulfide has a layer structure¹⁾ in which layers of TaS₂ composition are stacked one by one with van der Waals force. It is known that many bases and Lewis bases such as NaOH, pyridine etc. can be easily intercalated into the layer spacings to form a group of so called intercalation compounds^{2,3)}. Extensive studies for the intercalation compounds have been made on the physical properties such as super conductivity^{4,5)}. The chemical properties of them, however, have not been studied satisfactorily. For example, it has been suspected that, when metal hydroxide is intercalated, considerable amounts of water molecules also get into the layer spacings⁶⁾, but no thorough investigation has been made on it. There is no investigation on the thermal properties of the intercalation compounds either. In this report, we have studied the intercalation of hydroxides of alkali or alkaline earth metals into TaS₂. Particular attention has been focused upon the thermal behavior of the intercalation compounds as well as upon the relationship between intercalated water and crystal structure.

2 Experimental

Pure phase of α tantalum disulfide (α -TaS₂)

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was prepared by heating tantalum powder with sulfur vapor at about 900°C in a sealed quartz tube as described elsewhere⁷⁾. To obtain β -TaS₂, α -TaS₂ was ground to powder and, after the addition of a small amount of iodine, annealed at 600°C for 4 days and then at 500 °C for 2 weeks. Aqueous solutions of metal hydroxide were prepared with CO₂ free water and standardized before use.

The intercalation reaction was performed by suspending TaS₂ in the hydroxide solution under vigorous stirring. After the reaction, the suspension was filtered and the residue (Product) was washed repeatedly with deionized water before storage in a desiccator. The amount of intercalated hydroxide was determined by the neutralization analysis of the filtrate. The intercalation product was identified by X-ray powder diffraction (Rigaku-Denki, D-3 F) with CuK_α radiation. The sorption or desorption of water was measured gravimetrically with a silica balance. The thermal behavior was pursued either on an X-ray diffractometer attached with a high temperature apparatus, or by differential thermal analysis (DTA).

3 Results

3.1 Intercalation of metal hydroxides

An example of the intercalation reaction of NaOH into β -TaS₂ is shown in Fig. 1, where p denotes the molar ratio of the intercalated hydroxide to β -TaS₂. The reaction was rather rapid. Although an increase in reaction time increased the p value gradually, it also resulted

Fig. 1 Intercalation of NaOH into TaS_2 (22°C)
 p : Molar ratio of intercalated NaOH to $\beta\text{-TaS}_2$ ($\text{TaS}_2 \cdot p\text{NaOH}$), f_d : Fraction of decomposed TaS_2

in the decomposition of a part of TaS_2 to liberate free sulfide ions. The liberated sulfide ions were analyzed by iodometry and their fractions to total sulfur, f_d , are also shown in the same figure. The decomposition of TaS_2 was reduced either by decreasing the concentration of NaOH solution or by lowering the reaction temperature, but it was hardly prevented completely. Because of such decomposition the intercalation reaction was usually discontinued at 1.5 hr. The p value depended upon the reaction conditions, ranging from 0.18 to 0.33.

In this way, $\beta\text{-TaS}_2$ was intercalated with LiOH, NaOH, KOH, $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$. Typical X-ray diffraction patterns of $\beta\text{-TaS}_2$ and intercalation compounds are shown in Fig. 2. Intercalation caused significant expansion in layer spacing of the host structure as visualized by the lowering of diffraction angles (2θ) for (00 l) line. The observed hexagonal lattice parameters, a and c , of the intercalation compounds are listed in Table 1, which were in good agreement with those reported by Subba Rao *et al.*⁶⁾. It is remarkable that the expansion in layer spacing ($\Delta c/2$), falls in the range of either 5.74–5.91 Å (type I) or 2.92–2.99 Å (type II), depending upon the hydroxide intercalate. The expansion of type I was usually observed for the intercalation compound of NaOH or $\text{Ca}(\text{OH})_2$, while intercalation of LiOH, KOH, or $\text{Ba}(\text{OH})_2$ belonged to type II (Table 1 and Fig. 1). In some cases, however, the expansion was dependent on the conditions of intercalation. In the case of LiOH-intercalated compounds, for instance, preparation at room temperature gave type II, while a mixture of types I and II was obtained at 60°C.

Fig. 2 X-ray powder diffraction patterns of $\beta\text{-TaS}_2$ and intercalation products
 Type I: NaOH or $\text{Ca}(\text{OH})_2$ intercalated TaS_2 ,
 Type II: LiOH, KOH, or $\text{Ba}(\text{OH})_2$ intercalated TaS_2

Table 1 Lattice constants of intercalation products

Guest hydroxide	Lattice constants			
	a (Å)	c (Å)	$\Delta c/2$ (Å)	Type
LiOH	3.33	2×8.99	2.94	II
NaOH	3.31	2×11.96	5.91	I
KOH	3.32	2×9.04	2.99	II
$\text{Ca}(\text{OH})_2$	3.31	2×11.79	5.74	I
$\text{Ba}(\text{OH})_2$	3.30	2×8.97	2.92	II
host $\beta\text{-TaS}_2$	3.32	2×6.05		

As stated above, $\beta\text{-TaS}_2$ easily reacted with alkali or alkaline earth hydroxides giving two types of intercalation compounds. Unlike $\beta\text{-TaS}_2$, however, $\alpha\text{-TaS}_2$ was found to be quite inactive at room temperature, showing that the reaction is structure-sensitive. Even after a suspension of $\alpha\text{-TaS}_2$ in NaOH solution was heated to 160°C for 24 hr in a sealed quartz tube, a major part of $\alpha\text{-TaS}_2$ remained unchanged, with the rest having been converted into a mixture of types I and II.

3.2 Sorption of water

As mentioned above, the intercalation compounds have largely expanded layer spacings. To account for the large expansion, Subba Rao *et al.*⁶⁾ have proposed that the guest ions enter the layer spacing together with the water

Fig. 3 I-type $\rightarrow$ II-type transition of $\text{TaS}_2(\text{NaOH})_x(\text{H}_2\text{O})_y$ by evacuation
 $\circ$: $(002)_I$, $\bullet$: $(002)_{II}$

of hydration, and attempted to relate the large expansion in terms of the radii of hydrated ions. However, they neither measured the actual content of water, nor paid attention to the fact that the expansion can not vary continuously but is classified into two types. In this section, we examined the sorption of water in relation to the layer expansion.

It was found that the NaOH-intercalated compound, $\text{TaS}_2(\text{NaOH})_x$, which was prepared as type I structure, was converted into type II on evacuation at room temperature. Figure 3 shows the changes in X-ray diffraction intensity and diffraction angle for (002) lines. The diffraction angle (2θ) of type I structure was observed to increase a little in the initial stages, showing that the layer spacing of type I shrinks somewhat before the conversion. It is to be noted, however, that despite such preliminary phenomena the change of layer spacing from type I to II is essentially discontinuous.

The conversion $I \rightarrow II$ mentioned above is

Fig. 4 Sorption isotherms for $\text{TaS}_2\text{-MOH}$ complex at 25°C

likely associated with the decrease of water content of the sample. To confirm this, the sorption isotherms of water vapor were measured gravimetrically at 25°C for $\text{TaS}_2(\text{NaOH})_x$. As shown in Fig. 4, the isotherm distinctly shown an inflection at water vapor pressure ($P_{\text{H}_2\text{O}}$) of 8~10 Torr, though there were considerable hysteresis effects. The inflection of the isotherm indicates the occurrence of a phase transition, which was identified to be I (higher $P_{\text{H}_2\text{O}}$) $\rightleftharpoons$ II (lower $P_{\text{H}_2\text{O}}$) by X-ray diffraction analysis. The KOH-intercalated sample, which was prepared in type II, showed no such inflection at room temperature as shown in the same figure. These facts indicate that the layer spacings are largely dependent upon the water content. It is also noted that type II still contains considerable amounts of water at 25°C .

3.3 Thermal behavior of intercalation compounds

The structural change of intercalation compounds was studied by heating the samples in a high temperature apparatus attached to the X-ray diffractometer. The X-ray diffraction patterns for $\text{TaS}_2(\text{NaOH})_x$ are shown in Fig. 5. This compound exhibited $I \rightarrow II$ conversion

Fig. 5 Structural change of NaOH intercalation compound with heating in the high temperature camera
a: R.T. (type I), b: R.T. (after evac.) (type II), c: 50°C , d: 110°C (type III), e: 130°C (type IV), f: 160°C , g: 190°C (type V), h: 240°C , i: 500°C

by evacuation at room temperature as stated before. The subsequent heating was carried out in vacuo. With a rise in temperature up to 500°C, there appeared three phases stepwise as evidenced by the changes of diffraction patterns. We name these phases III, IV and V respectively. The diffraction lines of these phases could be indexed by assuming layer structure. The layer spacings (c) shrunk stepwise as listed in Fig. 5, and the layer expansions ($\Delta c/2$) for phase III, IV and V are 1.5 Å, 0.8 Å and 0.3 Å respectively.

The thermogravimetric (T.G.) analysis was carried out to determine how these phase transitions are related to the changes in water content of the samples. Figure 6 shows the T.G. curve for NaOH intercalated sample, together with the structural information obtained by the previous X-ray diffraction study. The NaOH intercalated compound showed steep weight losses at about 40°C and 120°C, which corresponded to I $\rightarrow$ II and III $\rightarrow$ IV transitions respectively. The weight decreased gradually up to 500°C, while the transition to the final type V went to completion at 240°C (see Fig. 5). The water content per mole of TaS_2 , Y , was determined on the basis of the dry weight at 500°C. It is thus seen that the lowest temperature phase, type I, contains more than 2 water molecules per TaS_2 ; the water content decreases with increasing temperature accompanied several phase transitions. The KOH intercalated compound exhibited a similar weight loss at about 100°C in vacuo, which was found to correspond to II $\rightarrow$ III conversion from X-ray diffraction study. In this case, however, heating above 150°C was not attempted.

3.4 Structure of intercalation compounds

As was stated in the foregoing sections, about 0.3 mol of hydroxides could be intercalated in TaS_2 , irrespective of the kind of hydroxides. The intercalation compounds thus formed were classified into two types, I and II, which had different layer spacings. On evacuation at room temperature, type I transformed into II, which on thermal dehydration was further converted stepwise into III, IV and V, the types of narrower layer spacings. It appears that the layer spacing is not associated directly with the kind

of guest hydroxide but determined by the amount of water introduced together. Figure 7 shows the increment of layer spacing, $\Delta c/2$, of each type of NaOH-intercalation compounds relative to that of pure $\beta\text{-TaS}_2$ as a function of the water content. Obviously $\Delta c/2$ increases almost in proportion to the water content except for type V, confirming the above estimation.

In what manner are such water molecules incorporated in the intercalation compounds? In connection with this question, Subba *et al.* have proposed that water is incorporated as the water of hydration of the guest ions. This proposal, however, encounters two difficulties. First, since the hydration number should depend on ionic species, the layer spacing should also depend on the guest hydroxides. In practice, however, any intercalation compound prepared in aqueous hydroxide solutions belongs to either type I or II, irrespective of the hydroxide used. Second, it is expected that dehydration from hydrated ions should proceed continuously on heating, and therefore, if the radii of hydrated ions determines the layer spacing, the layer spacing should shrink continuously on sample heating, in contrast to such abrupt changes of layer spacing as observed.

In this line of consideration, we propose that, while a part of the incorporated water exists as the water of hydration of guest ions, a major part is used for filling space between layers determining the layer spacing. It is suspected that the latter is not arranged at random in the layer space but maintains a certain degree of order and behaves like the water of crystallization. We presume that the discontinuous change of the layer spacing during dehydration

Fig. 6 TGA curve for $\text{TaS}_2(\text{NaOH})_x(\text{H}_2\text{O})_y$
 $P_{\text{H}_2\text{O}}=20$ torr, $Y=[\text{H}_2\text{O}]/[\text{TaS}_2]$

Fig. 7 Relation between water content (y) and increase in layer spacing ($\Delta c/2$) of $\text{TaS}_2 (\text{NaOH})_x (\text{H}_2\text{O})_y$
 $y = [\text{H}_2\text{O}]/[\text{TaS}_2]$

results from the reordering of the water of crystallization from one stable arrangement to another, just as seen for unusual crystalline hydrate.

From this point of view, suggestive is the correlation of Fig. 7 between $\Delta c/2$ and water content. The straight line going through the points for type I through IV intersects Y axis at about 0.5 mol H_2O per mol TaS_2 . This amount of water is not effective for the expansion of layer spacing and therefore assignable as the water of hydration of the guest ions. The remaining water, on the other hand, can be assigned as the water of crystallization determining the layer spacing. The amount of this kind of water are about 2, 1, 0.5 and 0.25 mol- H_2O per TaS_2 for types I through IV, respectively. It is noted that the amount is halved succeeding on going from a type to next. A corresponding change is observed in $\Delta c/2$. That is, the $\Delta c/2$ is 5.8, 2.9, 1.5 and 0.8 Å for types I through IV, respectively, becoming almost halved on going from I to II, and so on. For type V, which is no longer hydrated, $\Delta c/2$ is only about 0.3 Å. This shows that the dehydrated Na^+ and OH^- ions are located in the octahedral sites of TaS_2 , causing only a limited extent of layer expansion.

The relation between layer spacing and water content for type I through IV mentioned above seems to be understood most satisfactorily by assuming that each type represents a phase of so called stage compounds. The most well-known example of stage compounds has been provided by graphite-alkali metal systems.

Fig. 8 Stage compounds model for NaOH -intercalation compounds

d : Desorption amount of H_2O [layer]/ TaS_2 [layer]

A model for the stage compounds in the present is proposed in Fig. 8. For simplicity the structure is considered to be constructed with two building units, one the TaS_2 layer (shown by full lines) and the other the layer of the water of crystallization (shown by broken lines). The guest ions and its hydration water should be somewhere between the TaS_2 layers but are neglected in the drawing because they exert relatively minor effects structurally. In the proposed model, double H_2O layers and a single H_2O layer are inserted into each layer space of TaS_2 for types I and II, respectively, while for types III and IV a single H_2O layer inserted into every second and fourth layer space of TaS_2 , respectively. Thus, respective types correspond to stage 1/2, stage 1, stage 2 and stage 4 compounds.

According to the proposed model, the observed amount of water of crystallization for each type is easily accounted for by assuming that each H_2O monolayer consists of about 1 mol H_2O per 1 mol TaS_2 . Similarly, the observed expansion of layer spacing ($\Delta c/2$) for each type can also be understood by the model if the H_2O monolayer is about 3 Å thick. Without this sort of stage compound model, it is difficult to explain why the water content and the layer expansion decreases on dehydration in the characteristic manner as observed.

It is to be noted that the proposed model is consistent with the appearance of superlattice diffraction lines in the X-ray diffraction patterns for types III and IV. As understood from Fig. 8, all TaS_2 layers in type I or II are arranged in a symmetric way to keep an identical distance between two neighboring TaS_2 layers. This is not the case for types III and IV, where TaS_2 layers are not spaced uniformly, the ob-

served layer spacing, $c/2$, is simply an average of actual spacings. This implies that types III and IV are interpreted as "superlattice" structures with respect to the stacking of TaS_2 layers. This situation accounts for the appearance of (003) line for type III and (001/2) line for type IV in Fig. 5, which should be absent for a simple layer structure.

As mentioned above, the stage compounds model can be applied to the intercalation compounds very effectively. As compared with the stage compounds of graphite-alkali metal complexes, however, structural investigations to support this model are rather difficult because of poorer crystallinity of the compounds in this case. Further progress in this line of investiga-

tion is highly desirable.

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新しい電気化学

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本書は、電気化学協会創立 50 周年記念事業の一つとして編集委員会の奉仕により企画刊行されたもので、電気化学の基本的枠組みと現在の動向が初学者にも概観できるようにまとめられた入門的解説書であります。

エネルギー変換、電子材料、ライフサイエンスなどを軸にして、現在様相が一変しつつあるこの分野の新しい姿が豊富な図・写真・イラストにより平易に解説されています。

内容は次の通りで、高校生の課外活動、大学・高専のテキスト・参考書、技術者・研究者の指導書として利用願えれば幸いです。

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