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Preparation and thermal degradation behaviour of a layer-type complex consisting of TaS_2 and α-naphthylamine

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A layer-type complex TaS_2 (α-naphthylamine)$_{0.46}$ having a basal spacing of 2.2 nm was prepared by soaking a mixture of the components in an ampoule at 433 K for 25 to 35 days. This complex was resealed in an ampoule after purification, followed by γ-radiation and heating to 473 K. The resulting sample was again heated at various temperatures below 1273 K. On heating to 643 K, the inserted α-naphthylamine polymerized, although with some removal from the complex, with a decrease in basal spacing to 1.35 nm. Another complex appeared faintly simultaneously. This second complex with a basal spacing of 0.96 to 0.92 nm formed more abundantly on heating to 773 K and then decreased in amount at higher temperature. The complex decomposed at 1273 K to result in TaS_2. Such thermal degradation behaviour is discussed from the standpoint of preparation of the layer-type complex consisting of TaS_2 and carbon.

1. Introduction

The present authors have previously reported studies on the thermal degradation behaviour of the layer-type complexes of clay-α-naphthylamine [1] and of FeOCl and some organic compounds [2], in which the following results were described: (i) thermal stabilities of the host inorganic compounds layers were influenced in various ways by intercalating the guest organic compounds; (ii) the layer-type complexes consisting of inorganic compounds and carbon may be prepared by carbonizing organic compounds between the thermally stable inorganic compounds layers; (iii) organic compounds in such a situation act as a reducing agent to inorganic compound layers at the heat-treatment stage. The resulting decomposition products, therefore, were sometimes different from those derived from the host inorganic compounds. These results aroused our interest in connection with the development of new materials through heating a series of the layer-type complexes of inorganic and organic compounds.

It is known that a series of dichalcogenides readily form layer-type complexes with many organic compounds [3]. Among them, TaS_2 is of interest because of its superconductivity. Gamble *et al.* [4] succeeded in raising the superconducting transition temperature from 0.75 K for TaS_2 to 4 to 5 K by intercalating organic compounds. These phenomena led us to an attempt to prepare a layer-type complex consisting of TaS_2 and a carbon layer, because the carbon layer is regarded as the guest layer with a high π-electron density which must change the superconducting transition temperature. Fortunately, the decomposition temperature of TaS_2 is so much higher than 1273 K that it may be possible to carbonize the organic compounds between the TaS_2 layers [5].

The present work was carried out as a preliminary experiment to prepare the unique complex stated above. The purposes of this paper are to report the preparation and subsequent thermal degradation behaviour of a layer-type complex of TaS_2 and α-naphthylamine; and to discuss the possibility of preparing this complex.

2. Experimental details

About 2 g α-naphthylamine ($C_{10}H_9N$) and 1.5 g TaS_2 powders (under 44 μm) were sealed in an ampoule under vacuum, followed by retention

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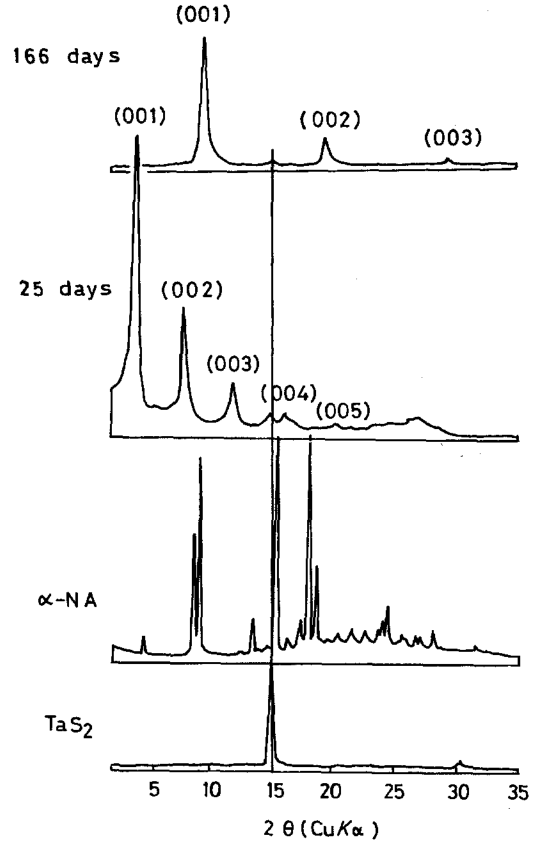

Figure 1 X-ray diffraction profiles of TaS_2, α-naphthylamine and the resulting complexes.

in a thermostat at 433 K for various periods in order to prepare the complex with a limited composition. α-naphthylamine and the resulting complex are abbreviated as NA and TNC, respectively. The complex with the limited composition was washed with acetone to remove NA attached to the TaS_2 powder surface and then resealed in an ampoule under vacuum to be used for subsequent treatments.

In order to polymerize NA in TaS_2 layers, the comples was γ-radiated by 12 Mrad, followed by heating to 473 K at 1 K min^{-1} and held for 1 h. The resulting complex was subsequently resealed separately in several ampoules (sample weight: ~ 0.1 g and ampoule volume: ~ 4 cm^3) to heat to 643, 773, 973 and 1273 K at a heating rate of 1 K min^{-1} for 1 h. Structural analyses were carried out using X-ray diffraction with Ni-filtered CuKα radiation, elemental analysis and scanning electron microscopic (SEM) observation. Elemental analysis, in particular, has so rarely been used in studies on such a subject that its results are expected to give valuable information. Gases evolved during the heat-treatment process were also identified using mass spectroscopy.

3. Results

3.1. Preparation and TaS_2–α-naphthylamine complex

Fig. 1 shows X-ray diffraction profiles of TaS_2, NA and the resulting complexes, for which analytical data are shown in Table I. After retention for 1 day, some peaks from TNC appeared strongly, although weak peaks of TaS_2 remained, and finally gave the profile shown in Fig. 1 after 25 days. This profile, as well as its analytical values, changed little until 35 days retention. This complex, called as TNC-1, has a basal spacing of 2.2 nm which is larger than that of TaS_2 by 1.6 nm. Its empirical formula was determined as $TaS_2(NA)_{0.46}$ from the analytical data in Table I. Through longer retention of 166 days, TNC-1 changed into another complex (TNC-2) of which the basal spacing was 0.95 nm. TNC-1, with the larger basal spacing, was used for subsequent heat treatment.

3.2. Heat treatment of TNC-1

Fig. 2 shows changes in the X-ray diffraction profiles of TNC-1 with heat treatment temperature (HTT). A slight amout of TaS_2 remained in the resulting complex. The peak intensities of the γ-radiated TNC-1 weakened remarkably without

TABLE I Some analytical data of TaS_2, α-naphthylamine and complexes

Sample	Basal spacing (nm)	Elemental analysis (wt %)				Atomic ratio		
		C	H	N	TaS_2†	H/C	N/C	C/Ta
TaS_2	0.602	–	–	–	–	–	–	–
α-naphthylamine (NA)	–	83.9*	6.3*	9.8*	–	0.09*	0.10*	–
Complexes 25 days	2.2	17.56	1.48	2.72	78.24	1.00	0.13	4.58
166 days	0.95	2.69	0.64	1.32	95.35	2.83	0.42	0.58

*Calculated values from molecular formula.
†wt % TaS_2 is the difference.

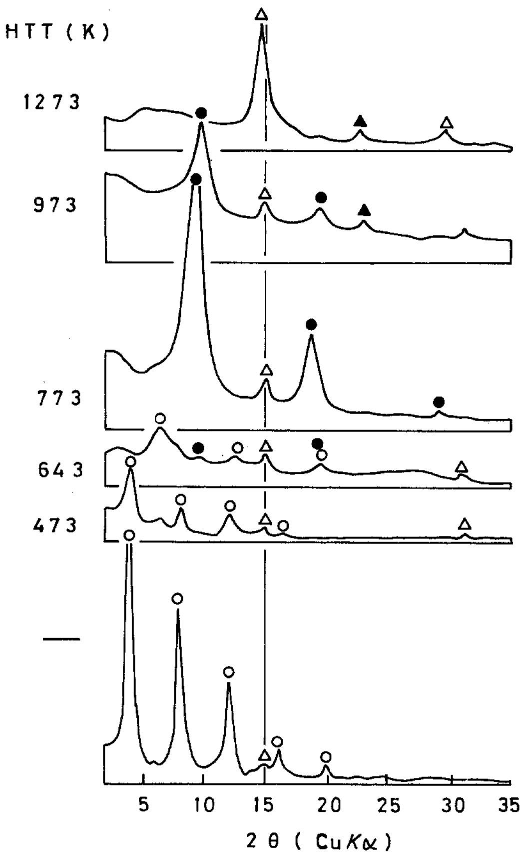

Figure 2 Changes of X-ray diffraction profiles of the complex TNC-1 with HTT (○: TNC-1, ●: TNC-2, △: TaS_2 and ▲: tantalum oxide).

shift in their diffraction angles upon heating to 473 K. On heating to 643 K, as shown in Fig. 2, the peaks further weakened with a shift towards higher diffraction angles corresponding to a basal spacing of 1.35 nm; additional peaks also appeared. These additional peaks became clear after heating to 773 K and it was decided that they resulted from the same structural complex as TNC-2. The basal spacing of 0.96 nm decreased to 0.92 nm after heating to 973 K. Upon heating to 1273 K, the complex decomposed resulting in TaS_2, although its diffraction is not as strong as that of the original TaS_2. A small peak, possibly from Ta_2O_5 or δ-TaO, appeared faintly.

Table II shows changes in basal spacing and atomic ratios of TNC-1 with HTT. The ratio C/Ta decreased remarkably up to ~ 643 K and then slightly at higher HTT. The ratio H/C, on the contrary, decreased slightly up to HTT of 773 K and more remarkably at higher HTT. The ratio N/C may be not so accurate because of a small content of nitrogen. However, it is reasonable to conclude that the ratio N/C decreased gradually with increasing HTT.

3.3. Identification of the evolved gases

The gases evolved from the complex in the glass tubing were identified using mass spectroscopy (Table III). H_2S was the main gas evolved on heating to 773 K. After heating to 973 K, CH_4 evolved abundantly in addition to H_2S. NH_3 and C_2H_2 or N_2 (possibly C_2H_2) were also detected. On heating to 1273 K, CH_4, H_2S and C_2H_2 or N_2 were evolved.

3.4. SEM observations

Fig. 3 shows raw TaS_2 crystals of plate (or disc) form, several microns thick and several 10 μm or less in diamater. Through the intercalation reaction with NA, however, TaS_2 crystals expanded, resulting in the accordion-like structure which can be seen in Fig. 4. An enlarged photograph of a typical example is shown in Fig. 5. The thickness of the expanded complex reached 20 μm. Fig. 6 shows the complex after heating to 973 K, in which the accordion-like structure is not so typical compared with those shown in Fig. 4. In Fig. 7, in which the 1273 K complex is shown, the faint accordion-like structure is observed without rupture of the layered structure.

4. Discussion

4.1. TaS_2-α-naphthylamine complex

The present work revealed that the TaS_2–NA

TABLE II Changes in some analytical data of the complex TNC-1 with HTT

HTT (K)	Basal spacing (nm)	Elemental analysis (wt %)				Atomic ratio		
		C	H	N	TaS_2*	H/C	N/C	C/Ta
Original	2.2	17.56	1.48	2.72	78.28	1.00	0.13	4.58
643	1.35	14.72	1.13	1.55	82.60	0.92	0.09	3.64
773	0.96	10.18	0.93	0.05	88.84	1.09	0.004	2.33
973	0.92	9.74	0.47	1.34	88.45	0.56	0.12	2.25
1273	–	10.61	0.28	0.37	88.74	0.31	0.03	2.44

*wt % TaS_2 is the difference.

TABLE III Evolved gases identified by mass spectra*

HTT (K)	H_2S	NH_3	CS_x†	CH_4	C_3H_8	C_2H_4 or N_2
643	100	3	5	–	–	1
773	100	2	–	12	–	4
973	62	15	–	100	1	14
1273	61	1	–	88	2	100

*Numbers are relative intensity.
†$x = 1$ and 2.

complex has the formula $TaS_2(NA)_{0.46}$ with a basal spacing of 2.2 nm (TNC-1), and this changes into another complex, TNC-2, having a basal spacing of 0.92 to 0.96 nm through further extended retention at 433 K or heating to 643 to 973 K. In view of the results of elemental analysis (Tables I and II), NA in TNC-2 must have decomposed, although its chemical composition is not so definite. Therefore, $TaS_2(NA)_{0.46}$ was only one complex between TaS_2 and NA. Gamble [6] has reported that TaS_2 intercalated with NA to result in the complex $TaS_2(NA)_{0.03}$ the basal spacing of which is 2.15 nm, though no details of its preparation conditions are given. Both TaS_2–NA complexes prepared in this work and by Gamble have equal basal spacings but their chemical formulae are significantly different. As a result, $TaS_2(NA)_{0.46}$ with a basal spacing of 2.2 nm was decided to be the limiting composition for this system. The configuration of NA between TaS_2 layers must be the same as that determined by Whittingham in view of their equal basal spacings [7].

4.2. Thermal degradation behaviour of $TaS_2(NA)_{0.46}$

X-ray diffraction peaks of the 473 K complex are situated at same angles as those of the original complex TNC-1, although they are broader giving evidence of considerable disorder. These must be attributable to disorders formed in TaS_2 layers as suggested by H_2S evolution and in the inserted NA layers.

The X-ray profile of the 643 K complex indicates the presence of two complexes: one appears to be TNC-1 with a basal spacing decreased by heating (symbol ○ in Fig. 2) and the other to be TNC-2 formed discontinuously from TNC-1 (symbol ● in Fig. 2). As suggested from changes in atomic ratio C/Ta and H/C, on heating to 643 K, the organic compounds polymerize in TaS_2 layers together with some removal from the layers. Evolution of low molecular compounds containing carbon atoms (e.g. C_2H_2, CS_x) are evidence to support rupture of the naphthalene ring and an increase in lattice defects in the TaS_2 layer.

TNC-2 formed more abundantly after heating to 773 K during which CH_4 and C_2H_2 were evolved. The basal spacing of this complex is 0.96 nm being larger than that of TaS_2 by 0.36 nm. Although 0.36 nm is very near to thickness of the carbon layer, the formation of a carbon layer in TNC-2 is denied by its elemental analysis shown in Tables I and II. The rupture of the naphthalene ring in NA is sure to be a requirement for TNC-2 formation.

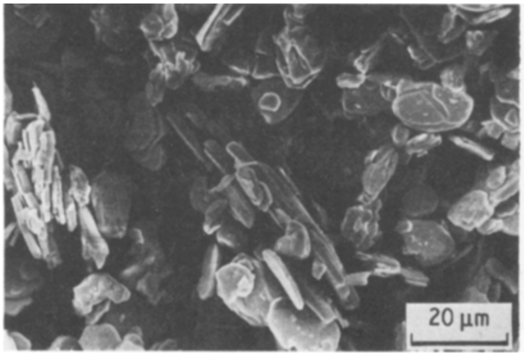

Figure 3 Scanning electron micrograph of raw TaS_2 crystals.

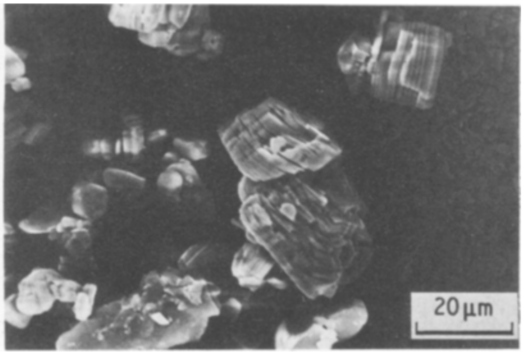

Figure 4 Scanning electron micrograph of $TaS_2(NA)_{0.46}$ (TNC-1), before heating.

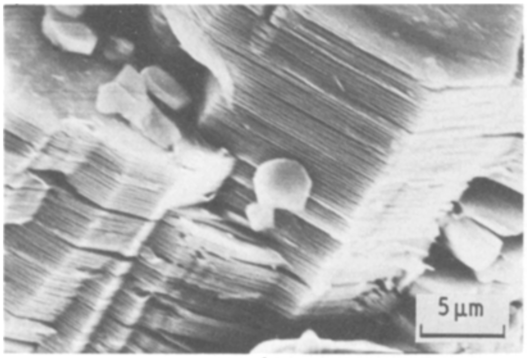

Figure 5 Scanning electron micrograph of a typical accordian-like structure of TNC-1, before heating.

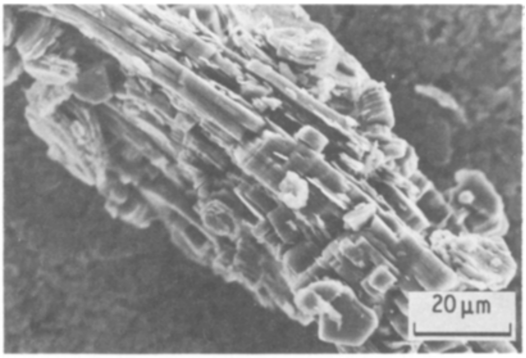

Figure 7 Scanning electron micrograph of TNC-1, after heating to 1273 K for 1 h.

The changes observed below 773 K continued to occur up to 973 K with a broadening of X-ray diffraction peaks and a decrease in basal spacing from 0.96 to 0.92 nm. Since TNC-2 did not remain at higher HTT, the basal spacing of TNC-2 must converge to 0.92 nm. A remarkable decrease in atomic ratio H/C suggests that organic compounds in the TaS_2 layers further polymerize at 973 K. The expanded accordian-like structure, though not so typical, was not degradated on conversion from TNC-1 to TNC-2.

After heating to 1273 K, TNC-2 disappeared and TaS_2 somewhat reformed. Analytical data of the 1273 K complex gives some characteristics of the thermal degradation behaviour of $TaS_2(NA)_{0.46}$: (i) the layer-type complexes studied previously decomposed thermally to result in the different complexes of original compounds [1, 2]. The present complex, however, formed the original compound TaS_2; (ii) at temperatures as high as 1273 K, the inserted materials were removed without reaction with the host TaS_2 layer; (iii) the 1273 K sample contains a considerably large amount of carbon in spite of the non-appearance of clear diffraction peaks from the complex. The carbon in this sample must be partly a very thin pyrolytic carbon layer formed on the sample powder surfaces and partly carbons constituting some complex with no presentation of clear diffusion peaks; in other words, a complex with a seriously disordered structure.

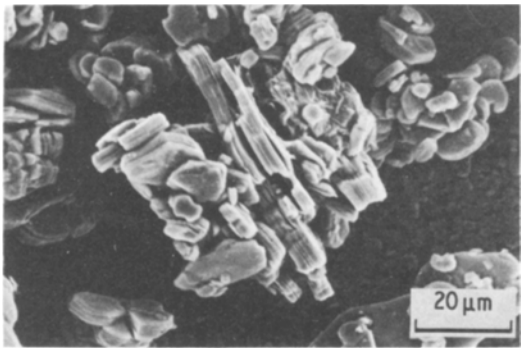

Figure 6 Scanning electron micrograph of TNC-1, after heating to 973 K for 1 h.

Although the complex decomposed after heating to 1273 K to reform TaS_2, a layer-type complex remained below HTT of 973 K. Elemental analysis indicated that α-naphthylamine in TaS_2 layers considerably polymerized (carbonized). These phenomena suggest a possibility of preparing the layer-type complex consisting of TaS_2 and carbon through developing the method to suppress the removal of the inserted NA up to higher HTT. Thompson [8] has found that addition of sulphur to the intercalate both orders and thermally stabilizes the resulting TaS_2–pyridine complex. Sulphur also acts as a dehydrogenation reagent through evolution of H_2S, leading to favourable polymerization of organic compounds. This technique, therefore, may be useful in preparing our intended complex. At 1273 K, tantalum oxide formed slightly together with TaS_2. Heat treatment under a reducing atmosphere may be also useful in preparing such a complex.

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