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Studies on the Hexagonal Hydrate of Molybdenum Trioxide. The Physical Properties of the Hydrate and Its Changes on Heat Treatments in Air, in Hydrogen, and in a Hydrogen–thiophene Mixture

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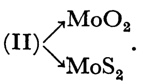
The hexagonal hydrate(I) of molybdenum trioxide, which has been newly found and reported, was studied by X-ray diffraction analysis, IR and NMR spectroscopies, and by other methods. Also studied was the change in (I) on heat treatments in air, in hydrogen, and in a hydrogen–thiophene mixture. The crystal was found to belong to a hexagonal system. The air-dried sample has about 0.46 mol of water. This water is included as a water molecule, not as hydroxyl. By the dehydration of (I), anhydrous molybdenum trioxide (I′), which has the same crystal structure as (I), is obtained. Another new form of (I′) is the hexagonal trioxide, which is hygroscopic and which easily absorbs water when standing in air. This (I′) is metastable and is irreversibly transformed to rhombic molybdenum trioxide(II) at 420—430 °C. In hydrogen and in a hydrogen–thiophene mixture, reduction and sulfurization occur in addition to transformation, which can be shown schematically as: (I)→(I′)→



$(\mathrm{II})\genfrac{}{}{0pt}{}{\nearrow \mathrm{MoO_2}}{\searrow \mathrm{MoS_2}}$

. Transformation in hydrogen and in the hydrogen–thiophene mixture proceeds faster than in air. Reduction occurs more quickly in the hydrogen–thiophene mixture than in hydrogen.

Molybdenum trioxide is usually prepared by the calcination of hydrate, the so-called molybdic acid or ammonium salt. Many works have been reported on the hydrates of molybdenum trioxide[1–4] and hydrates.[5–10] Among the hydrates of molybdenum trioxide, though only a rhombic MoO_3 is well known.[4] In addition to the rhombic MoO_3, there are several oxides the composition of which are very close to MoO_3, such as Mo_4O_{11},[11] Mo_8O_{23},[12] and Mo_9O_{26}.[12] All of these oxides show specific deep colours. As for the hydrate, the yellow dihydrate has been studied by many workers[5–10] and its precise structure was recently determined by Krebs.[13] Besides, yellow monohydrate and white monohydrate were found, but their precise natures have not yet been reported.

In a previous paper,[14] the present author reexamined in detail the nature of these hydrates of molybdenum trioxide. In these studies, a new form of hydrate, with a hexagonal structure, was found. By heat treatment, this new hydrate was transformed to anhydrous trioxide, which has the same structure as the initial hydrate. This anhydrous trioxide has never been reported, either. This hydrate and this oxide have smaller densities than other oxides and show interesting properties.

In the present paper, the author will report on his research into the precise physical properties of the hexagonal hydrate by X-ray diffraction analysis, IR and NMR spectroscopies, and by other methods. Also reported on will be research into their changes on heat treatments in air, in hydrogen, and in a hydrogen–thiophene mixture, this research was undertaken with a view to revealing the natures of the hydrate when used as a catalyst.

Experimental

Preparation of the Hexagonal Hydrate. The new hydrate of molybdenum trioxide was prepared by precipitation from a saturated ammonium paramolybdate solution by the addition of conc. HNO_3, to give an acidity of 2—3 M at about 70 °C. (HCl can be also used instead of HNO_3.) The sample (denoted as 'Sample A') was dried in air at room temperature.

To obtain an ammonia-free sample (denoted as 'Sample B'), the precipitate was prepared from a saturated sodium molybdate solution under the same conditions as the sample A. It probably contains a small amount of sodium ions, unlike Sample A, which contains ammonium ions.

X-Ray Diffraction, IR, and NMR Studies. The precise methods of the X-ray diffraction analysis, and IR and NMR spectroscopies were described previously.[14] Electron microscopic observation was carried out with a scanning-electron microscope (JAPAN ELECTRONICS LAB.-JSM U3 Type).

Measurements on Heat Treatments. Diffrential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed in air. The rate of weight decrease was measured by means of a quartz spring balance[15] with helices 15 mm in diameter and with 135 turns, with a capacity of 2 g and with a sensitivity of 0.1 mg/div. After heat treatment at each temperature, the sample was subjected to X-ray diffraction analysis, IR spectroscopy, and chemical analysis.

The behavior of the sample upon heat treatment in atmospheric hydrogen and in the hydrogen–thiophene mixture was studied in the same way. The purified hydrogen flowed at a rate accurately controlled to 0.1 mol/hr by means of a needle valve and an auxiliary regulator. The thiophene was fed into a stream of hydrogen by means of a calibrated hypodermic pump, at the feed rate of 1.4×10^{-2} mol/hr.[16]

Analysis of Ammonia and Sulfur. The ammonia was analyzed by the Kjeldahl method[17] and the sulfur, gravimetrically by the $BaSO_4$ method.[18]

Results

Air-dried Sample A. The X-ray pattern of the sample A, as shown in Fig. 1 (this pattern is not seen on the ASTM cards), belongs to a hexagonal system with a lattice constant of a=6.09Å and c=9.14Å. The indecies and the calculated spacings of lattice planes are listed in Table 1. Observation by the scanning-electron microscope also shows that the crystal belongs to the hexagonal system, as is shown in the photo.

The amount of ammonia in the air-dried sample A was about 1.6%, according to chemical analysis, this value corresponds to 0.15 mol of NH_3 per mol of MoO_3. According to thermogravimetric analysis, the sample has 0.54 mol of water per MoO_3, therefore, the

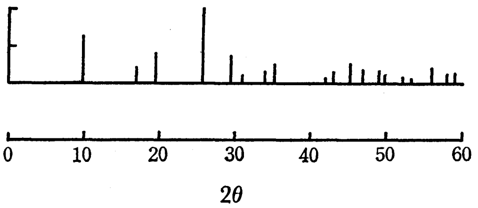


Fig. 1. The X-ray diffraction pattern of the sample A.

TABLE 1. THE X-RAY DIFFRACTION DATA OF THE SAMPLE

Index	d Spacings Calcd	d Spacings Obsd	Intensity
001	9.14	9.12	0.49
100	5.27	5.31	0.14
002 101	4.57	4.57	0.30
102	3.45	3.46	1.00
110 003	3.05	3.02	0.48
111	2.89	2.89	0.06
200 103	2.64	2.64	0.09
201 112	2.53	2.54	0.34
113	2.15	2.16	0.05
104	2.10	2.10	0.13
203 210	1.99	1.99	0.20
211	1.95	1.95	0.14
		1.86	0.14
114 212 122	1.83	1.83	0.08
300	1.76	1.76	0.04
301	1.73	1.73	0.05
213	1.67	1.67	trace
302	1.64	1.64	0.21
		1.59	0.13
		1.57	0.07

composition can be represented as $(NH_3)_{0.15} \cdot MoO_3 \cdot 0.54\,H_2O$ or $(NH_4)_{0.15} \cdot MoO_{3.08} \cdot 0.46\,H_2O$. However, the amounts of ammonia and water are indefinite and vary slightly with the conditions of preparation.

As can be seen from Fig. 2, which shows the IR spectrum of the A sample, the intensities of the bands at 3478 and 1610 cm^{-1} decrease when heated at a temperature below 300 °C, the bands can be attributed to the OH stretching and deformation vibrations of hydrated water respectively. The band at 1610 cm^{-1} shows that the water is present as water molecules, not as hydroxyl. The bands at 3170 and 1409 cm^{-1} agree exactly with the frequencies of the stretching and deformation vibrations of the ammonium ion.[19,20]

In the range below 1000 cm^{-1} of Mo-O-bond stretching and bending vibrations and of the librational motion of H_2O, the sample has a relatively sharp band at 976 cm^{-1}, a broad band at 916 cm^{-1}, a shoulder at 869 cm^{-1}, and a broad absorption in the range from 750 cm^{-1} to 450 cm^{-1}.

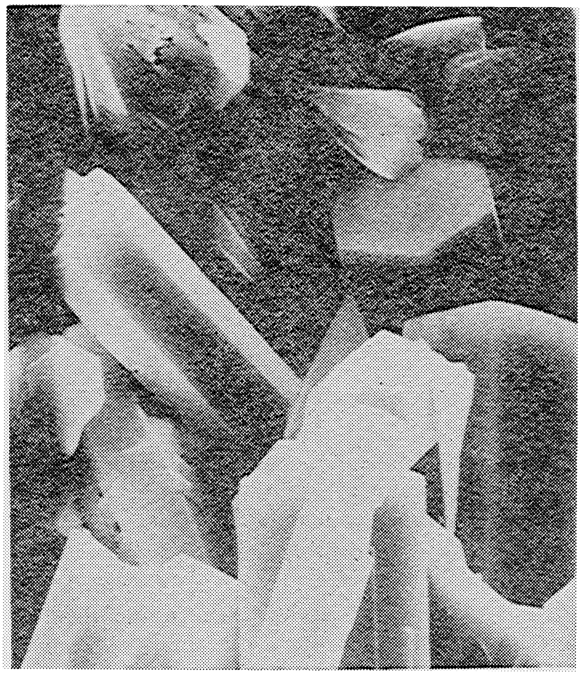


Photo. The sample A observed by the scanning electron microscope (×6000).

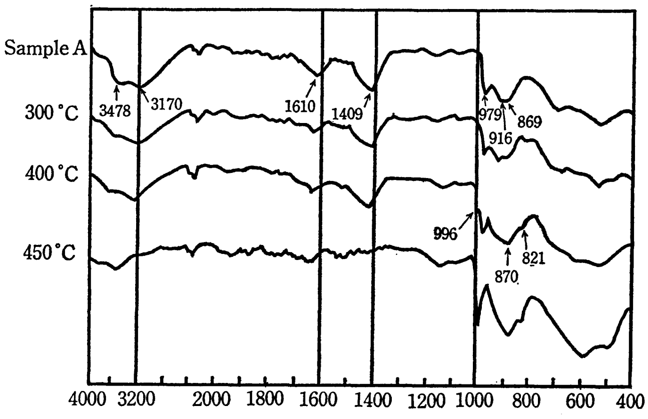


Fig. 2. IR spectra of the sample A.

The NMR absorption was measured at room temperature and at that of liquid nitrogen. The peak-to-peak values of the A sample at the temperature of liquid nitrogen, as shown in Fig. 3, are 1.4 G (I) and 11.7 G (II) respectively. (The values are the mean of at least five measurements.) As has been reported in a previous paper,[14] the peak-to-peak value of the II band may be attributed to absorption by the water molecule. The I band is attributed to the ammonium ion, which is mobile at the temperature of liquid nitrogen (probably in flip-flop motion).

The number of protons contained as water molecules was determined by free induction decay after a 90° pulse at 10 MHz; it agreed well with the value obtained by chemical and thermal analyses.

The density of the sample A was determined pycnometrically with cyclohexane at 25 °C. The density of the sample A is 3.73 g/cm^3, and that of the anhydrous hexagonal trioxide is 3.58 g/cm^3. These values are smaller than the 4.175 g/cm^3 of rhombic MoO_3[21] and the 6.47 g/cm^3 of MoO_2,[4] and are closer to the 3.117 g/cm^3 of the yellow dihydrate.[13]

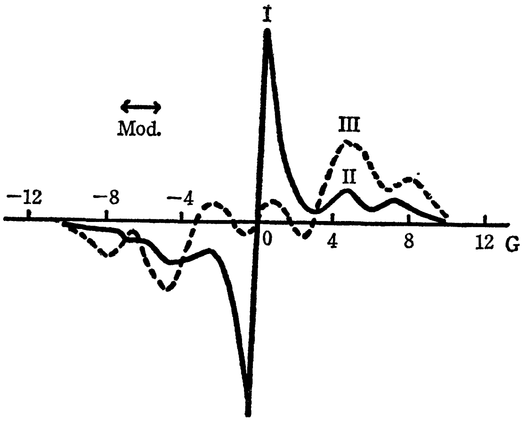


Fig. 3. NMR spectra of the samples A and B at liquid nitrogen temperature.
——: sample A, ----: sample B.

Air-dried Sample B. The B sample from sodium salt gives an X-ray diffraction pattern identical with that of the sample A except for a small difference in intensity.

The IR spectrum of the B sample is identical with that of the A sample except for the disappearance of the bands due to the ammonium ion.

The peak-to-peak value (III) of the NMR derivative curve of the B sample at the temperature of liquid nitrogen, which is also shown in Fig. 3, is nearly equal to that of the II band of the A sample and is due to the water molecule. In the case of the B sample, no band due to the ammonium ion was observed.

The X-ray and IR spectra show that the B sample is exactly the same compound as the A sample. The B sample probably contains a small amount of the sodium ion, unlike the A sample, which contains the ammonium ion, but the fact that the crystal structures are identical seems to show that these ions are contained as impurities in the crystal.

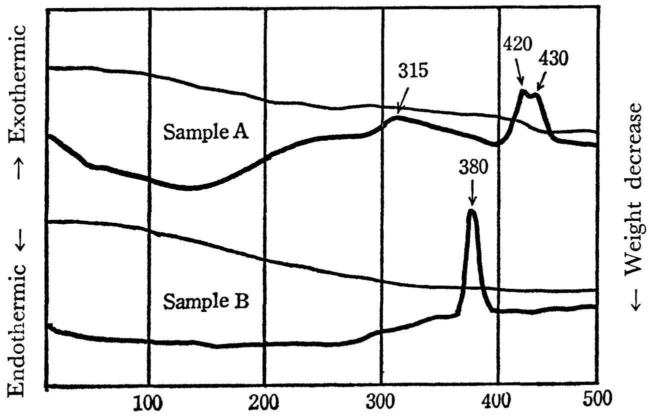


Fig. 4. DTA-TGA curves of the samples A and B.
—: DTA, —: TGA

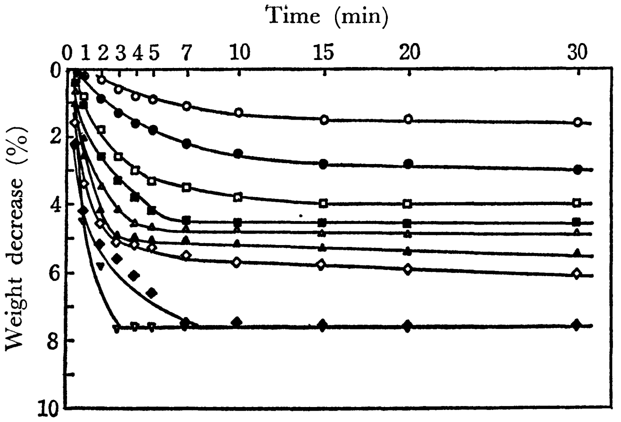


Fig. 5. Isothermal curves of weight decrease of the sample A by heat treatment in air.
○: 100 °C, ●: 150 °C, □: 200 °C, ■: 250 °C, △: 300 °C, ▲: 350 °C, ◇: 400 °C, ◆: 450 °C, ▽: 500 °C.

Behavior on Heat Treatment in Air. The DTA-TGA measurement of the A sample was done up to 500 °C. As can be seen from the typical DTA-TGA curve shown in Fig. 4, the weight of the sample decreases continuously up to 300 °C, without any definite decomposition temperature, which corresponds to 0.46 mol of H_2O per mol of MoO_3. At 315 ° and 420—430 °C, an exothermal transformation, accompanied by a small weight loss, is observed. The transformation temperature, however, was not reproducible, because, for samples from different lots, one to three exothermal peaks appeared in the range from about 300 to 430 °C.

Figure 5 shows the rate of the weight loss measured in air at various temperatures by means of a quartz spring balance. At every temperature below 300 °C, the rate of weight loss rapidly decreases for several minutes, while the weight is kept nearly constant by further heating. The weight loss is about 5% at 300 °C. By heating at a temperature above 300 °C, after an initial rapid weight loss of about 5%, the weight exponentially approaches a certain minimum value, which is quickly attained by 450 and 500 °C heating. Thus, these curves seem to show weight decreases by two different processes—one below 300 °C and the other above 300 °C. These two processes correspond exactly to the endothermal change at the temperature below 300 °C and the exothermal transformation above 300 °C, observed on the DTA-TGA curve, respectively.

The quantities of ammonia included in the A sample heated for 30 min at various temperatures, as determined

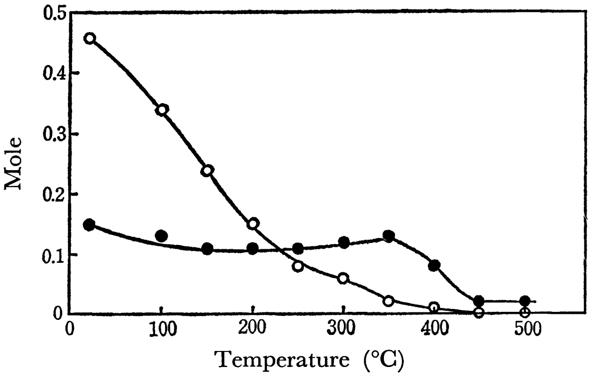


Fig. 6. Amounts of ammonia and water in the sample A after 30 min heating.
●: ammonia, ○: water.

TABLE 2. THE RESULTS OF X-RAY DIFFRACTION ANALYSIS OF THE SAMPLE A AFTER HEAT TREATMENTS, IN AIR, IN HYDROGEN AND IN A HYDROGEN–THIOPHENE MIXTURE

Time (min)		5	10	20	30	40	60	100	180	360
Air	350 °C	I	I	I	I	I	I	I	I	I+II
	400 °C	I	I	I	I+II		I+II		II	
Hydrogen	350 °C	I	I			I	I*+II+III	II+III		
	400 °C		I*+II+III			II+III				
Hydrogen + thiophene	350 °C	I+II	I+II	II+III		III				
	375 °C	I+II	II+III	III						
	400 °C	II+III	III							

I(I′); hexagonal oxide, II; rhombic MoO_3, III; MoO_2, *; trace

by chemical analysis, are plotted against the heating temperature in Fig. 6. The amount of ammonia content decreases slightly at below 150 °C, probably because of the desorption of the absorbed ammonia, is kept nearly constant up to 350 °C, and begins to decrease above 350 °C. The amount of residual water in the heated sample, as calculated from the total weight loss and the weight loss due to the deammoniation, is also shown in Fig. 6, on the assumption that the ammonia was contained as ammonium ions.

According to the above results, the weight loss below 300 °C is mainly to the liberation of the hydrated water, and the small weight decrease accompanied by the exothermal transformation at 420—430 °C in the DTA-TGA measurement is due to deammoniation. However, as the deammoniation must be endothermic, the transformation at 420—430 °C is essentially a solid-phase transformation. The small deammoniation is, therefore, considered to be an evolution of an ammonia impurity induced by the crystal rearrangement.

In the case of the B sample also, it evolves water as does the A sample below 300 °C and undergoes an exothermal transformation at about 380 °C, as is shown in Fig. 4, but no detectable weight loss is observed.

The results of the X-ray diffraction analysis of the A sample treated in air are summarized in Table 2. No change is observable in the diffraction pattern on heating at 350 °C for 360 min, even though most of the hydrated water is liberated in several minutes at that temperature, showing the conversion of the hydrated sample A (I) to anhydrous hexagonal oxide (I′). After 360 mins' heating at the same temperature, a weak pattern of rhombic MoO_3(II) is detectable. At 400 °C, II appears in 30 min; the X-ray pattern gradually increases in intensity as the duration of heating increases.

In the previous paper,[14] the present author reported that the transformation of I′ to II was observed at 420—430 °C. However, a small exothermal peak appears at 315 °C on the DTA curve. The X-ray studies show that a small amount of II is observed when I′ is heated in air at 350 °C for 360 min. It may, therefore, be assumed that the small peak at 315 °C can be the transformation of I′ to II.

I′ below the transformation temperature is highly hygroscopic, as is clearly shown by the fact that it absorbs easily about half of the water in heating. On the other hand, the sample heated above the transformation temperature absorbs water only slightly.

The IR spectra of the sample after heat treatment are shown in Fig. 2. The IR absorption bands at 3478 and 1610 cm^{-1} due to H_2O sharply decrease in intensity below 300 °C. The bands at 3170 and 1409 cm^{-1} due to the ammonium ion are retained up to near 350 °C, the intensities begin to decrease temperatures above 400 °C, as is to be expected from the results of thermal analysis, while the bands below 1000 cm^{-1} do not show any appreciable change at 300 °C. Above 400 °C, new bands at 996, 876, and 821 cm^{-1} due to II appear, and at 450 °C the spectrum changes completely to that of II.

Heat Treatment in Hydrogen (Reduction). The A sample was treated in hydrogen under an atmospheric pressure at 350 °C and 400 °C, and the structural changes were observed by X-ray diffraction (see Table 2). At 350 °C, no change is observable for 40 min, but at 60 min the intensity of the original hexagonal pattern is markedly reduced and patterns due to II and MoO_2(III) appear. At 100 min, most of the sample is reduced to III. A similar change is observable at 400 °C, though the rate is steep.

According to the X-ray results, II always coexists with the III phase. This suggests that no abrupt reduction of I′ to III occurs; rather, the reduction passes through II—that is, I′→II→III.

Heat Treatment in the Hydrogen-thiophene Mixture. The changes in the A sample in the hydrogen–thiophene mixture were studied at 350, 375, and 400 °C. In this case, the hydrodesulfurization of thiophene also takes place, and the sample acts as a catalyst for the reaction. The results of the X-ray diffraction analysis of the A sample are listed in Table 2.

As in hydrogen, the transformation to II and the reduction to III also occur. II appears before III is detected. This fact suggests, as in the case of hydrogen, that the reaction proceeds in this sequence: I′→II→III. In the hydrogen–thiophene mixture, however, the transformation and reduction proceed far more quickly than in hydrogen. II, for example, appears in 5 min at 350 °C, and III, in 20 min. The change is even faster at higher temperatures.

The sulfur contents of the A sample when treated in the hydrogen–thiophene mixture were analyzed by the $BaSO_4$ method. Though MoS_2 was not detected by X-ray diffraction analysis, the sulfur contents increased with the time of treatment, as is shown in Fig. 7. The sulfurization did not exceed 5%, however, the rate of sulfurization was slower than those of transformation and reduction. As III was not easily sulfurized

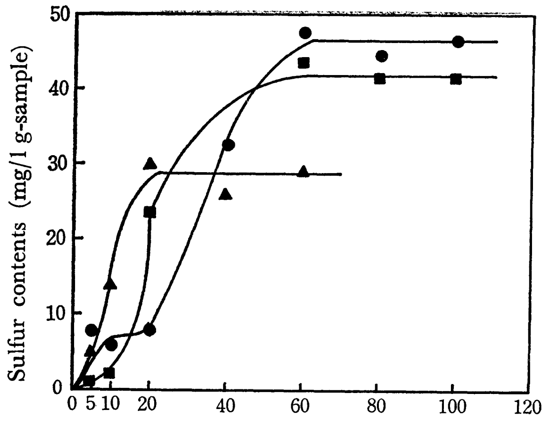


Fig. 7. Sulfur contents in the sample A after heat treatment for 30 min in a hydrogen-thiophene mixture. ●: 350 °C, ■: 375 °C, ▲: 400 °C.

under the same conditions,[16] II was assumed to selectively sulfurized in this experiment.

Discussion

As has been described above, I′, with the same hexagonal crystal structure as I, is obtained by dehydration. Neither I nor I′ have ever been reported previously; they may, then, be regarded as a new form.

The results of IR and NMR spectroscopies show that the water included in I is contained as water molecules, not as hydroxyl. The fact that I′ has the same crystal structure as I means that I′ has a structure with vacancies, in which the water molecule can be occluded.

The postulation of this structure is supported by the following facts: (i) I has no definite decomposition temperature upon dehydration. (ii) I′ is highly hygroscopic, in contrast with the nonhygroscopic nature of II. (iii) The density, when the substance A treated in air, changes from 3.75 g/cm^3 of I to 3.58 g/cm^3 of I′, without any change in the crystal structure.

I′ is surely transformed to II at 420—430 °C. II is not, on the other hand, transformed to I′ on cooling, and, so is regarded as a stable phase at low temperatures. I′ is, therefore, a metastable phase, and the transformation at 420—430 °C is from a metastable to a stable phase. The variation in the transformation temperature is probably due to the above fact. As has previously been described, the transformation is always accompanied by the decomposition of a small amount of ammonium ions. At the same time, the endothermal deammoniation overlaps the exothermal change. The exothermal change in the DTA curve is, therefore, somewhat compensated for by the endothermal deammoniation. This is another reason for the irreproducibility of the DTA curve. In the case of the B sample, which is free from ammonium ions, the transformation shows a simple single exothermal peak, with no endothermal change. Such impurities as the ammonium ion or the Na$^+$ ion, which may be contained in the vacancies of the oxide, are assumed to stabilize the hexagonal phase; therefore, the transformation temperature may have something to do with the amount of such impurities.

In addition to dehydration, the reduction and sulfurization of I′ occur in hydrogen and in the hydrogen-thiophene mixture. It is clear from Fig. 5 that the dehydration proceeds more quickly than the reduction and the sulfurization. Thus, it may be concluded that the reduction and the sulfurization occur after dehydration.

On the other hand, the X-ray results suggest, as has been described previously, that the reduction occurs consecutively as I′→II→III.

Sulfurization also occurs along with reduction in the hydrogen–thiophene mixture. As has been described previously, it is assumed that II is preferentially sulfurized. Consequently, in the hydrogen–thiophene mixture I changes as is shown in Fig. 8. The X-ray diffraction analysis confirms that the I′→II transformation in hydrogen proceeds faster than in air, and that, in the hydrogen–thiophene mixture, the transformation proceeds much faster still. An interesting fact is that the existence of hydrogen or thiophene accelerates the I′→II transformation. The precise mechanism is not known, but it seems to be certain that these gases have some catalytic function in the transformation.

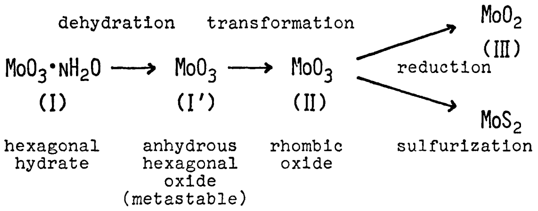


Fig. 8. Changes of the state of the hydrate by heat treatment, in air, in hydrogen and in a hydrogen-thiophene mixture.

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