JOURNAL OF CATALYSIS 58, 409–418 (1979)

Phase Diagram of the System Bi_2O_3–MoO_3

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Received August 19, 1977; revised August 4, 1978

The phase diagram of the Bi_2O_3–MoO_3 system was studied by X-ray diffraction and differential thermal analysis, in particular in the range Bi/Mo = 2/1 ∼ 2/3 of interest for catalysis. X-Ray diffraction identified the following eight compounds: $7Bi_2O_3 \cdot MoO_3$, $3Bi_2O_3 \cdot MoO_3$, low and high temperature forms of $3Bi_2O_3 \cdot 2MoO_3$, koechlinite, and high temperature forms of $Bi_2O_3 \cdot MoO_3$, $Bi_2O_3 \cdot 2MoO_3$, and $Bi_2O_3 \cdot 3MoO_3$. The low temperature form of $3Bi_2O_3 \cdot 2MoO_3$ is a new modification of the Bi/Mo = 3 compound, while $7Bi_2O_3 \cdot MoO_3$ corresponds to that reported hitherto as $\sim 10Bi_2O_3 \cdot MoO_3$, and others are identical to those found before. $Bi_2O_3 \cdot 3MoO_3$ forms eutectics with MoO_3 at 615°C and with $Bi_2O_3 \cdot 2MoO_3$ at 640°C. $Bi_2O_3 \cdot 2MoO_3$ is generated by the peritectic reaction of the liquid phase and the high temperature phase of $Bi_2O_3 \cdot MoO_3$ at 665°C. $Bi_2O_3 \cdot 2MoO_3$ is stable in the range from 665 to 540°C, below which it disproportionates into $Bi_2O_3 \cdot 3MoO_3$ and the koechlinite form of $Bi_2O_3 \cdot MoO_3$. The high temperature form of $Bi_2O_3 \cdot MoO_3$ is also formed by the peritectic reaction of the liquid and the high temperature phase of $3Bi_2O_3 \cdot 2MoO_3$. The transition temperatures between two modifications in $Bi_2O_3 \cdot MoO_3$ and in $3Bi_2O_3 \cdot 2MoO_3$ are supposed to be 600 and 750°C, respectively. $3Bi_2O_3 \cdot MoO_3$ forms a eutectic with $3Bi_2O_3 \cdot 2MoO_3$ at 950°C, and a solid solution with Bi_2O_3.

INTRODUCTION

Mixed oxides of the Bi_2O_3–MoO_3 system are widely used as one of the most effective catalysts in the partial oxidation of olefins to produce unsaturated aldehydes, unsaturated nitriles, or dienes. The catalytic activity and selectivity of this system are supposed to arise from the formation of oxy-salt or bismuth molybdate (*1*). Many investigations have already been devoted to the crystal chemistry of this system. However, the phase diagram has not yet been established even in the range of composition Bi/Mo = 2/1 ∼ 2/3 with high catalytic activity.

Belyaev and Smolyaninov (*2*) studied the phase diagram, and found three compounds of the following formulas: $3Bi_2O_3 \cdot MoO_3$ (mp 990°C), $Bi_2O_3 \cdot MoO_3$ (mp 970°C), and $Bi_2O_3 \cdot 3MoO_3$ (mp 648°C). They reported that $3Bi_2O_3 \cdot MoO_3$ formed solid solutions with Bi_2O_3 and with $Bi_2O_3 \cdot MoO_3$, and that $Bi_2O_3 \cdot 3MoO_3$ formed eutectics with $Bi_2O_3 \cdot MoO_3$ at 636°C and with MoO_3 at 618°C. Bleijenberg *et al.* (*3*) also reported these three compounds in their phase diagram, but they suggested that $3Bi_2O_3 \cdot MoO_3$ formed eutectics with Bi_2O_3 as well as with $Bi_2O_3 \cdot MoO_3$.

In addition to these three compounds, Erman *et al.* (*4*) found a new compound

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with the atomic ratio Bi/Mo = 1, or $Bi_2O_3 \cdot 2MoO_3$, and suggested that this compound was formed from the liquid by a peritectic reaction. Afterward they confirmed this reaction at 650°C by examining the detailed phase diagram (*5*). Kohlmuller and Badaud (*6*) and Chen and Smith (*7*) also reported the peritectic reaction for the formation of $Bi_2O_3 \cdot 2MoO_3$ in their phase diagrams. However, Batist *et al.* (*8*) and Grzybowska *et al.* (*9*) indicated that this compound is unstable and disproportionates into $Bi_2O_3 \cdot 3MoO_3$ and $Bi_2O_3 \cdot MoO_3$ at temperatures below 550°C. Thus $Bi_2O_3 \cdot 2MoO_3$ may be stable only in a relatively narrow temperature range. However, its stable range was not described in any diagrams reported hitherto.

As to the compound $Bi_2O_3 \cdot 3MoO_3$, many workers concluded that $Bi_2O_3 \cdot 3MoO_3$ is a congruently melting compound. On the other hand, Erman *et al.* (*5*) reported the peritectic reaction, liq. + $Bi_2O_3 \cdot 2MoO_3 \rightarrow Bi_2O_3 \cdot 3MoO_3$, at 640°C. Their endothermic effect, however, was claimed by Chen and Smith (*7*) to be a spurious peak related to the migration of molten material during thermal cycling.

For the compound of Bi/Mo = 2, it is generally recognized that there exist two modifications (*1, 4*): koechlinite form (K-form) (*10*) and high temperature form (H-form) (*11*). However, Erman and Gal'perin (*12*) reported another modification as an intermediate phase in the transition from K- into H-form. Thus, there remain some discrepancies about the transition between both modifications.

The situation is more complicated in the range Bi/Mo = 1/0 ~ 2/1, where besides $3Bi_2O_3 \cdot MoO_3$ (*2, 3, 13*) some other compounds were reported: $\sim 10Bi_2O_3 \cdot MoO_3$ (*6, 13*), $2Bi_2O_3 \cdot MoO_3$ (*14*), and the compound with the composition Bi/Mo = 1.3 ~ 1.5 (*15, 5, 7*). Two diagrams reported before (*4, 6*) of this range are very different from each other.

Thus, the phase diagram of the system Bi_2O_3–MoO_3 has not yet been precisely established. The establishment of the phase diagram is very important not only for a fundamental understanding of catalytic properties, but also for research and development of highly active catalysts. The present paper is concerned with the phase diagram in particular in the range Bi/Mo = 2/1 ~ 2/3 which seems to be the most promising for catalytic applications.

EXPERIMENTAL METHODS

The phase diagram was studied mainly by X-ray diffraction analysis and differential thermal analysis (DTA). X-Ray diffraction was carried out by a Rigaku diffractometer with scintillation counter, and Ni-filtered CuKα radiation was used. DTA measurement was performed with a Rigaku Micro-DTA instrument in the range of 500 to 1050°C at a heating and cooling rate of 0.625, 1.25, 2.5, or 5.0°C/min. A tall lidded Pt cell was used to avoid the appearance of spurious peaks pointed out by Chen and Smith (*7*). The sample size was 50 ~ 200 mg. The temperatures of melting, eutectic, and peritectic points were determined from those at the foot of the peak in cooling curve. The stable temperature range of the compound $Bi_2O_3 \cdot 2MoO_3$ was determined by examining the solid state reaction between $Bi_2O_3 \cdot MoO_3$(K) and $Bi_2O_3 \cdot 3MoO_3$ at 500 ~ 600°C. The amount of $Bi_2O_3 \cdot 2MoO_3$ formed was measured by X-ray diffraction analysis on the quenched sample after reaction. The transition temperature between the K- and H-form of the compound $Bi_2O_3 \cdot MoO_3$ was also determined in a similar manner as above.

A large number of samples were prepared at intervals of 1 atom% Mo in composition. They were obtained by coprecipitation at pH = 7 from the mixture of appropriate amounts of Bi_2O_3 solution

TABLE 1

X-Ray Diffraction Analysis of the Sample with the Composition Bi/Mo = 2/1 ~ 0/1

Sample Bi/Mo ratio	Phase composition[a]		
	Calcination temperature (°C)		
	500	580	650
2/1	2/1(K)	2/1(K)	2/1(H)
2/1 ~ 1/1	2/1(K) + 2/3	2/1(K) + 1/1	2/1(H) + 1/1
1/1	2/1(K) + 2/3	1/1	1/1
1/1 ~ 2/3	2/1(K) + 2/3	1/1 + 2/3	1/1 + 2/3
2/3	2/3	2/3	2/3
2/3 ~ 0/1	2/3 + MoO_3	2/3 + MoO_3	2/3 + MoO_3

[a] 2/1(K)—$Bi_2O_3\cdot MoO_3$(koechlinite), 2/1(H)—$Bi_2O_3\cdot MoO_3$ (high temperature form), 1/1—$Bi_2O_3\cdot 2MoO_3$, 2/3—$Bi_2O_3\cdot 3MoO_3$.

in conc HNO_3 and MoO_3 solution in conc NH_4OH, followed by evaporation to dryness and calcination at 500 ~ 650°C for 10 hr. Bi_2O_3 and MoO_3 used as starting materials were prepared by the thermal decomposition of bismuth nitrate $Bi(NO_3)_3\cdot 5H_2O$ and ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, respectively, at 600°C for 20 hr in air. For some compositions, the samples were also prepared by sintering of Bi_2O_3 and MoO_3 at 600°C for 20 hr in air. However, DTA curves as well as X-ray diffraction patterns were almost the same regardless of the preparation method.

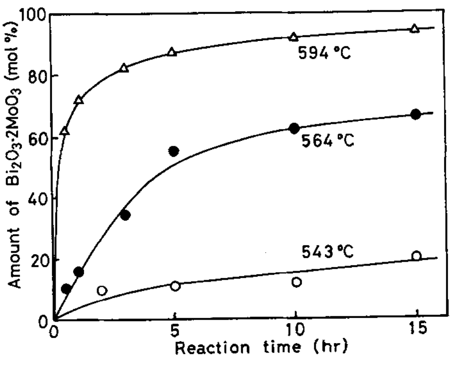

FIG. 1. Formation of $Bi_2O_3\cdot 2MoO_3$ from $Bi_2O_3\cdot MoO_3$(K) and $Bi_2O_3\cdot 3MoO_3$.

RESULTS AND DISCUSSION

1. *Binary Oxide Compounds between Bi_2O_3 and MoO_3*

First, X-ray diffraction analyses were performed on many samples with various compositions to check on the compounds reported before, such as $Bi_2O_3\cdot 3MoO_3$ (*16, 17*), $Bi_2O_3\cdot 2MoO_3$ (*4, 7*), and $Bi_2O_3\cdot MoO_3$ (*7, 10, 11*). The results on samples with the composition Bi/Mo = 2/1 ~ 0/1, calcined at 500, 580, and 650°C, are shown in Table 1. From these results, it is confirmed that there exist four phases: two kinds of $Bi_2O_3\cdot MoO_3$ (koechlinite and high temperature forms), $Bi_2O_3\cdot 2MoO_3$, and $Bi_2O_3\cdot 3MoO_3$, as reported before (*1, 4*).

The specimen Bi/Mo = 1/1 calcined at 500°C consisted of the mixture of $Bi_2O_3\cdot MoO_3$(K) and $Bi_2O_3\cdot 3MoO_3$, while it changed into the single compound of $Bi_2O_3\cdot 2MoO_3$ after calcination at 580 and 650°C. Thus, $Bi_2O_3\cdot 2MoO_3$ could be obtained only by calcining at higher temperatures in the present work, where the samples were prepared via evaporation to dryness after the coprecipitation at pH = 7. If the coprecipitate was filtered after pH adjustment to 2 ~ 5, $Bi_2O_3\cdot 2MoO_3$ could be obtained via drying and calcining at

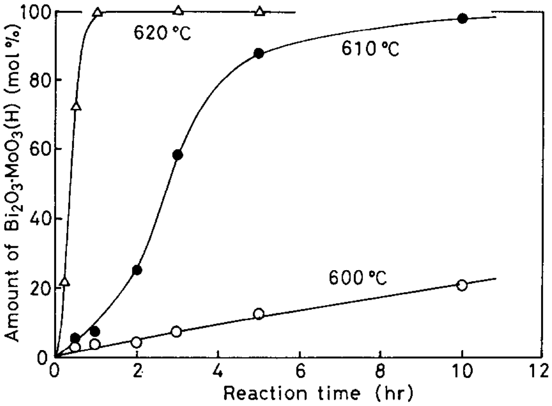

FIG. 2. Phase transition from koechlinite into the high temperature form of $Bi_2O_3 \cdot MoO_3$.

400 ~ 500°C (*8, 9, 18*). At these temperatures, however, it is unstable and decomposes into $Bi_2O_3 \cdot 3MoO_3$ and $Bi_2O_3 \cdot MoO_3(K)$ after prolonged heating (*8, 9*). Grzybowska *et al.* (*9*) indicated that this compound can be formed stably above 550°C. To confirm this, the solid state reaction between $Bi_2O_3 \cdot MoO_3(K)$ and $Bi_2O_3 \cdot 3MoO_3$ was reexamined at 500 ~ 600°C. Figure 1 shows the amount of $Bi_2O_3 \cdot 2MoO_3$ formed, which was determined from the X-ray diffraction intensities of the quenched samples after the reaction for certain periods. From this result, it is seen that the formation of $Bi_2O_3 \cdot 2MoO_3$ occurs above 540°C in good agreement with the report of Grzybowska *et al.* (*9*). The decomposition of this compound was also reexamined in the range of 450 ~ 550°C. As a result, this compound was found to be unstable and to disproportionate into $Bi_2O_3 \cdot MoO_3(K)$ and $Bi_2O_3 \cdot 3MoO_3$ on prolonged heating below 530°C, in accordance with the data of

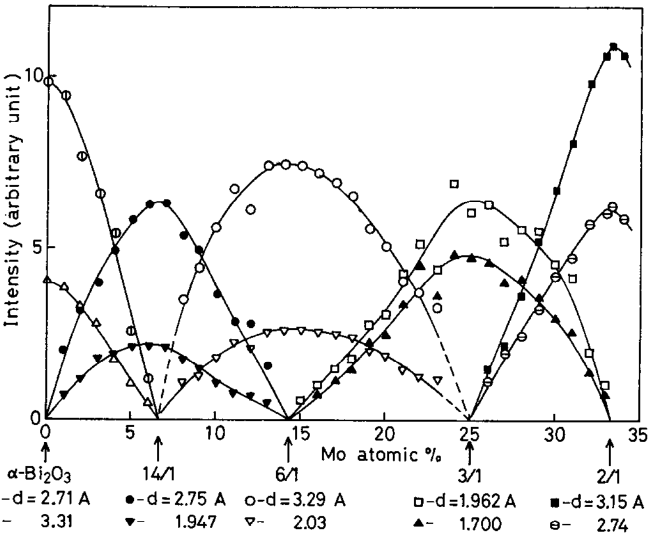

FIG. 3. The composition dependence of the intensities of some X-ray diffraction lines. Samples were calcined at 600°C for 10 hr.

TABLE 2

X-Ray Diagrams of $7Bi_2O_3 \cdot MoO_3$ and Two Modifications of $3Bi_2O_3 \cdot 2MoO_3$

$7Bi_2O_3 \cdot MoO_3$		$3Bi_2O_3 \cdot 2MoO_3$(L)		$3Bi_2O_3 \cdot 2MoO_3$(H)	
d(A)	Int.	d(A)	Int.	d(A)	Int.
7.782	4	8.580	7	12.04	18
3.805	2	3.655	1	11.41	12
3.581	1	3.436	1	9.428	16
3.226	100	3.240	100	6.046	7
3.079	2	2.875	7	5.695	11
2.887	17	2.851	9	3.746	6
2.753	26	2.821	18	3.424	6
2.625	1	2.728	19	3.307	77
2.591	2	2.560	2	3.235	85
2.510	4	2.504	6	3.185	8
1.994	25	2.357	1	3.148	7
1.947	9	2.009	9	3.033	6
1.883	1	1.978	8	2.937	65
1.727	12	1.962	17	2.899	18
1.668	16	1.897	1	2.826	12
1.614	7	1.725	5	2.680	100
1.557	1	1.715	5	2.501	10
1.468	1	1.708	5	2.384	16
1.444	1	1.700	11	2.065	14
1.425	1	1.658	9	2.015	54
1.377	2	1.620	6	1.997	6
		1.541	1	1.969	14
		1.413	1	1.950	42
		1.365	2	1.912	8
				1.771	7
				1.738	12
				1.728	10
				1.650	18
				1.626	17

Batist *et al.* (*8*) and Grzybowska *et al.* (*9*). Thus, it is concluded that $Bi_2O_3 \cdot 2MoO_3$ is formed stably above 540°C.

The phase transition of the K-form into the H-form of the compound $Bi_2O_3 \cdot MoO_3$ was investigated at 500 ~ 650°C in a similar manner as the formation reaction of $Bi_2O_3 \cdot 2MoO_3$ from $Bi_2O_3 \cdot MoO_3$(K) and $Bi_2O_3 \cdot 3MoO_3$. The transition occurred at higher temperatures than 600°C as shown in Fig. 2, but not at lower temperatures. Therefore, the transition temperature is concluded to be just 600°C. This result is roughly consistent with the observation of Batist *et al.* (*1*) that the K-form was obtained when the specimen was heated at 500 and 600°C while the H-form resulted on heating at 680 and 750°C. The present investigation, however, could not identify the intermediate phase which was reported during the transformation from the K- into the H-form by Erman and Gal'perin (*12*). The reverse transition of the H- into the K-form was also examined at 500 ~ 600°C, but no change was observed, probably because of its very slow rate. Another possible explanation of this irreversible transformation is that the K-form is a metastable phase and only the H-form is a stable phase thermodynamically.

In the range Bi/Mo = 1/0 ~ 2/1, four compounds were reported: $\sim 10Bi_2O_3 \cdot MoO_3$ (*6*, *13*), $3Bi_2O_3 \cdot MoO_3$ (*13*), $2Bi_2O_3$

$\cdot MoO_3$ (*14*), and $3Bi_2O_3\cdot 2MoO_3$ (*15*) [see also Refs. (*5*) and (*7*)]. But there exist some discrepancies among authors. Therefore, the crystal chemistry in this composition range was reinvestigated. Figure 3 shows the composition dependence of the intensities of some characteristic X-ray diffraction lines of each compound which appeared in the samples calcined at 600°C. Figure 3 points out undoubtedly the existence of three compounds with the atomic ratios Bi/Mo = 14/1, 6/1, and 3/1 in addition to α-Bi_2O_3 and $Bi_2O_3\cdot MoO_3$(K). All samples with the intermediate composition between every two neighboring compounds exhibited the diffraction lines indicating the mixture of two corresponding compounds.

Our diffraction pattern of the Bi/Mo = 14/1 compound given in Table 2 is closely similar to that of $\sim 10Bi_2O_3\cdot MoO_3$ reported by Kohlmuller and Badaud (*6*) though the composition is somewhat different. The compound reported before may be $7Bi_2O_3\cdot MoO_3$, since if it is $\sim 10Bi_2O_3\cdot MoO_3$ the maximum intensity should come at the position of 4.8 atom% Mo in Fig. 3. The presence of the compound with Bi/Mo = 6/1, or $3Bi_2O_3\cdot MoO_3$, has been generally recognized by many authors (*1*, *2*). The Bi/Mo = 3/1 compound coincides with $3Bi_2O_3\cdot 2MoO_3$ reported by Miyazawa *et al.* (*15*) in terms of composition. However, the X-ray diffraction pattern shown in Fig. 4a was quite different from theirs and also from those of the phase $Bi_{2x}Mo_{(1-x)}O_3$ (x = 0.55 ~ 0.62) reported by Kohlmuller and Badaud (*6*). Furthermore, heating at high temperatures changed this compound into another modification. The X-ray diffraction pattern of a quenched sample after heating to 900°C or after melting in Fig. 4 was well consistent with that of Miyazawa *et al.* (*15*). It may be spontaneously assumed, therefore, that the lines indicated by filled circles in Fig. 4 are assigned to the high temperature form of $3Bi_2O_3\cdot 2MoO_3$ while those indicated by open circles belong to the low temperature form. The latter is a new modification of the compound $3Bi_2O_3\cdot 2MoO_3$. By heating at 700°C, a part of the low temperature phase changed into the high temperature form, but the complete transformation was achieved only above 850°C. This behavior offers a difficulty in determining the transition temperature precisely, but it is supposed to be about 750°C from the temperature where both modifications can exist in the same amount. The X-ray powder diagrams of two phases of $3Bi_2O_3\cdot 2MoO_3$ are listed in Table 2.

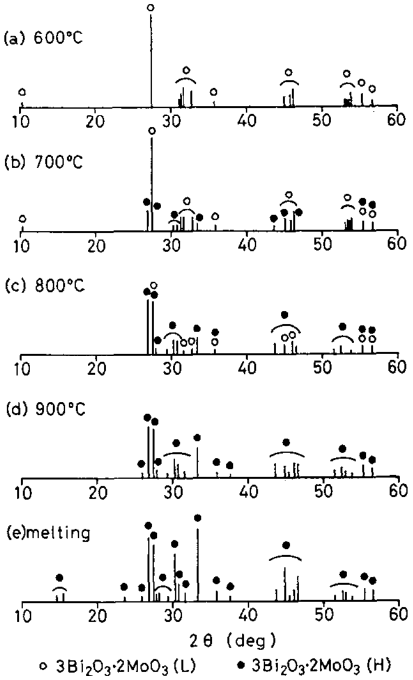

FIG. 4. X-Ray diffraction patterns (CuKα) of Bi/Mo = 3/1 samples quenched after heating at 600, 700, 800, and 900°C for 5 hr, and after melting.

2. Phase Diagram

Figure 5 shows some typical thermograms by DTA. The phase composition of the sample before and after DTA measurement is given in Table 3.

The thermogram of $Bi_2O_3\cdot 3MoO_3$ gave one peak not only in the heating run but also in the cooling run, in accordance with

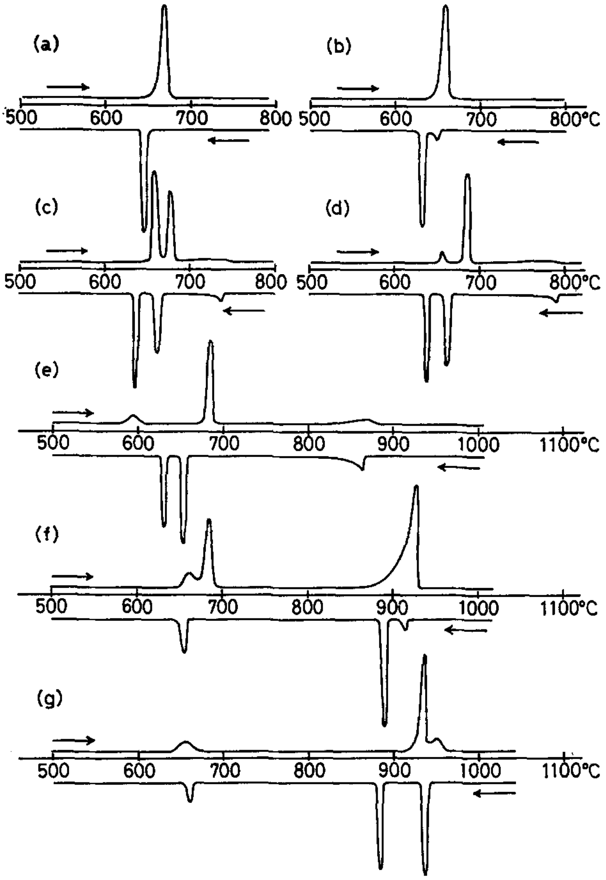

FIG. 5. Typical DTA curves. (a) Bi/Mo = 40/60, (b) 43/57, (c) 47/53, (d) 50/50, (e) 55/45, (f) 63/37, and (g) 66.7/33.3. Samples were calcined at 580°C for 10 hr except Bi/Mo = 55/45 at 500°C.

the result of Chen and Smith (7). The temperature at the foot of the peak agreed well in both runs. Therefore, these peaks are considered to be related to the fusion and the solidification, respectively. This result supports the conclusion that $Bi_2O_3 \cdot 3MoO_3$ is a congruently melting compound (*2*, *3*, *6*, *7*). The compound $Bi_2O_3 \cdot 2MoO_3$ showed three peaks, indicating complicated phase changes besides fusion or solidification. Their assignment will be mentioned later in this section. The mixture of $Bi_2O_3 \cdot 3MoO_3$ and $Bi_2O_3 \cdot MoO_3$(K) revealed an additional small peak near 590°C (see heating curve of Fig. 5e), which may be assigned to the formation of $Bi_2O_3 \cdot 2MoO_3$ from $Bi_2O_3 \cdot 3MoO_3$ and $Bi_2O_3 \cdot MoO_3$(K) though the temperature is somewhat higher than the result of Fig. 1 because of the slow reaction rate. For the sample Bi/Mo = 66.7/33.3 the situation is also rather complicated as shown by Fig. 5g. The small peak at about 650°C in the heating curve is reasonably assigned to the transition from the K- into the H-form though the temperature is somewhat higher than the result of Fig. 2.

The phase diagram based on the X-ray diffraction and the differential thermal analyses is presented in Fig. 6. In this diagram, the liquidus, the eutectic horizontal, and the peritectic horizontal were determined from the cooling curves, the temperature being adopted at the foot of

TABLE 3

Phase Composition of the Samples in Fig. 5 before and after DTA Measurement

Sample Bi/Mo ratio	Phase composition[a]	
	Before	After
40/60	2/3	2/3
43/57	1/1 + 2/3	1/1 + 2/3
47/53	1/1 + 2/3	2/1(H) + 1/1 + 2/3
50/50	1/1	2/1(H) + 1/1 + 2/3
55/45	2/1(K) + 2/3	2/1(H) + 1/1 + 2/3
63/37	2/1(K) + 1/1	3/1(H) + 3/1(L) + 2/1(H) + 1/1
66.7/33.3	2/1(K)	3/1(H) + 3/1(L) + 2/1(H) + 1/1

[a] 2/3—$Bi_2O_3 \cdot 3MoO_3$, 1/1—$Bi_2O_3 \cdot 2MoO_3$, 2/1(K)—$Bi_2O_3 \cdot MoO_3$ (koechlinite), 2/1(H)—$Bi_2O_3 \cdot MoO_3$ (high temperature form), 3/1(L)—$3Bi_2O_3 \cdot 2MoO_3$ (low temperature form), 3/1(H)—$3Bi_2O_3 \cdot 2MoO_3$ (high temperature form).

peak. The formation line of $Bi_2O_3 \cdot 2MoO_3$ from $Bi_2O_3 \cdot 3MoO_3$ and $Bi_2O_3 \cdot MoO_3$(K) was based on the result of Fig. 1, and the phase transition lines in $Bi_2O_3 \cdot MoO_3$ and $3Bi_2O_3 \cdot 2MoO_3$ were due to the results of Figs. 2 and 4, respectively. The compounds $3Bi_2O_3 \cdot 2MoO_3$, $3Bi_2O_3 \cdot MoO_3$, and $7Bi_2O_3 \cdot MoO_3$ may have a considerable solid solubility as suggested in the literature (*5–7*). In Fig. 6, however, the regions for these compounds are simply indicated by the lines since they are considered to be relatively narrow from the results of Fig. 3.

$Bi_2O_3 \cdot 3MoO_3$ forms a eutectic with MoO_3 at 615°C and at 71 atom% Mo.

$$\text{liq.} \rightarrow Bi_2O_3 \cdot 3MoO_3 + MoO_3. \qquad (1)$$

It is obvious from Fig. 6 that $Bi_2O_3 \cdot 3MoO_3$ also forms a eutectic with $Bi_2O_3 \cdot 2MoO_3$ at 640°C and at 59 atom% Mo (*6*, *7*), though it was considered to form a eutectic with $Bi_2O_3 \cdot MoO_3$ in some previous published work (*2*, *3*).

$$\text{liq.} \rightarrow Bi_2O_3 \cdot 3MoO_3 + Bi_2O_3 \cdot 2MoO_3. \qquad (2)$$

Figure 6 also shows that $Bi_2O_3 \cdot 2MoO_3$ is stable only in the relatively narrow temperature range of 665 ~ 540°C. That is, $Bi_2O_3 \cdot 2MoO_3$ is formed by the peritectic

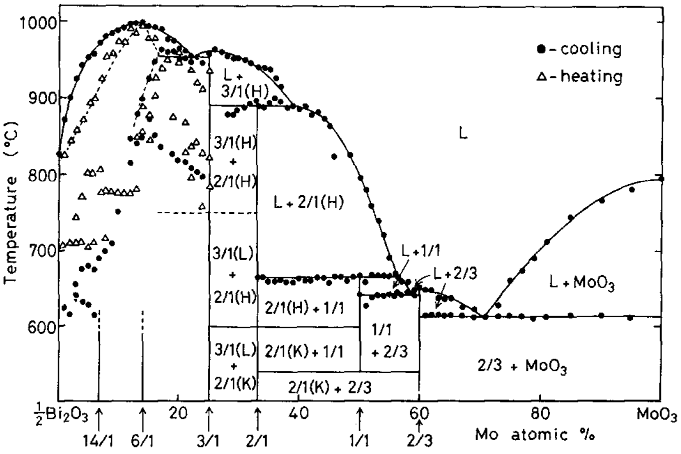

FIG. 6. Phase diagram of the system Bi_2O_3–MoO_3.

reaction of liquid MoO_3 with the high temperature form of $Bi_2O_3 \cdot MoO_3$ at 665°C (*5–7*),

$$MoO_3(liq.) + Bi_2O_3 \cdot MoO_3(H) \rightarrow Bi_2O_3 \cdot 2MoO_3. \quad (3)$$

but disproportionates into $Bi_2O_3 \cdot MoO_3(K)$ and $Bi_2O_3 \cdot 3MoO_3$ below 540°C (*8*, *9*).

$$2[Bi_2O_3 \cdot 2MoO_3] \rightarrow Bi_2O_3 \cdot MoO_3(K) + Bi_2O_3 \cdot 3MoO_3. \quad (4)$$

Since the rate of reaction (4) is very slow, however, $Bi_2O_3 \cdot 2MoO_3$ can exist even at room temperature as a metastable phase.

The formation of $Bi_2O_3 \cdot MoO_3(H)$ from liquid is also due to the peritectic reaction as in the case of $Bi_2O_3 \cdot 2MoO_3$ (*5*, *7*). The solid which takes part in this reaction is indicated to be the high temperature form of $3Bi_2O_3 \cdot 2MoO_3$.

$$MoO_3(liq.) + 3Bi_2O_3 \cdot 2MoO_3(H) \rightarrow 3[Bi_2O_3 \cdot MoO_3(H)]. \quad (5)$$

The high temperature phase of $Bi_2O_3 \cdot MoO_3$ should be transformed into the koechlinite form at 600°C. However, this transition could not be observed under the condition of the DTA measurement because of the slow reaction rate. Therefore, $Bi_2O_3 \cdot MoO_3(H)$ can exist even at room temperature. On the other hand, the transition between the low and high temperature forms of $3Bi_2O_3 \cdot 2MoO_3$ seems to occur reversibly. The transition temperature was suggested to be about 750°C from the result of Fig. 4.

Thus, the phase diagram could be established considerably in the range Bi/Mo = 0/1 ∼ 3/1. Differential thermograms in a cooling run of all samples with the composition in this range could be well accounted for by this phase diagram. Three exothermic peaks at 741, 668, and 640°C of the specimen Bi/Mo = 47/53 in Fig. 5 can be assigned to the precipitation of $Bi_2O_3 \cdot MoO_3(H)$ as primary crystal, the peritectic reaction (3), and the eutectic reaction (2), respectively. The heat effect due to the disproportionation reaction (4) was not observed for the reason mentioned above. Three peaks at 794, 667, and 641°C for the specimen Bi/Mo = 50/50 and those at 864, 657, and 633°C for Bi/Mo = 55/45 can also be related to the same phase changes. In the latter two cases, it is expected from the phase diagram in Fig. 6 that no exothermic peak should appear corresponding to the eutectic reaction (2). The cooling DTA curves in Fig. 5, however, showed fairly large exothermic peaks in both specimens. This contradiction can be explained as follows. The peritectic reaction (3) could not be completed under the conditions of the DTA measurement because the secondary crystal formed generally envelops the first crystal. The liquid residue would undergo the eutectic reaction (2) which leads to the appearance of an exothermic peak at 641°C for Bi/Mo = 50/50 or at 633°C for Bi/Mo = 55/45. These pretended heat effects in the Bi-richer range than Bi/Mo = 50/50 are not plotted in Fig. 6 to avoid confusion.

In the range Bi/Mo = 3/1 ∼ 1/0 the situation is very complicated. Heat effects observed in DTA were merely plotted in the phase diagram. These DTA results are inconsistent with the diagram of Erman *et al.* (*5*) and with that of Kohlmuller and Badaud (*6*). Thus, there remain many problems to be solved. However, the following conclusions might be deduced in this Bi-rich range from the present work.

(i) There exist two binary oxide compounds: $3Bi_2O_3 \cdot MoO_3$ and $7Bi_2O_3 \cdot MoO_3$.

(ii) $3Bi_2O_3$ forms a eutectic with the high temperature form of $3Bi_2O_3 \cdot 2MoO_3$ at about 950°C.

(iii) $3Bi_2O_3 \cdot MoO_3$ forms a solid solution with Bi_2O_3 in accordance with the conclusion of Belyaev *et al.* (*2*) and with the suggestion of Levin and Roth (*19*).

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