

The Relative Stabilities of Bi_2MoO_6 Polymorphs

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The relative stability of Bi_2MoO_6 polymorphs was studied by isothermal heating at 250–635°C, and 100–1500 kg/cm². The results obtained follow: (1) A reversible transition was observed between two stable phases at low (L) and high (H) temperatures, $\gamma(\text{L})\text{-Bi}_2\text{MoO}_6$ with the koechlinite structure and $\gamma(\text{H})\text{-Bi}_2\text{MoO}_6$ (= γ' labeled by Elman). (2) A pressure–temperature phase diagram of Bi_2MoO_6 was drawn and it showed that the $\gamma(\text{L})$ -form was more stable than the $\gamma(\text{H})$ -form in the low-temperature and high-pressure region. (3) The transition temperature of $\gamma(\text{L}) \rightleftharpoons \gamma(\text{H})$ under atmospheric pressure was estimated to be about 570°C by extrapolation of the phase boundary. (4) A third modification, $\gamma''\text{-Bi}_2\text{MoO}_6$ (a metastable phase), was not detected in the experiments. A free-energy–temperature diagram for the three modifications, $\gamma(\text{L})$, $\gamma(\text{H})$, and γ'' , is proposed on the basis of the present experimental results and previously published data. © 1985 Academic Press, Inc.

Introduction

The bismuth molybdate-based system is one of the most important heterogeneous catalyst used for the selective oxidation and ammoxidation of olefins. Therefore, the phase equilibria and compounds of the $\text{Bi}_2\text{O}_3\text{-MoO}_3$ system have been the subject of several studies (1–5).

Bi_2MoO_6 , one of the compounds, shows curious polymorphism. Recently, a review on its polymorphism was published, and it showed that there are many inconsistencies in the number of the modifications, in their relative stabilities, and in the phase-transition temperatures (6). These discrepancies may be caused by an irreversible transition between the γ - and γ' -phases. When $\gamma\text{-Bi}_2\text{MoO}_6$ is heated above about 640°C under atmospheric pressure, the transition from

the γ -phase to the γ' -phase can be observed easily, but on cooling, the reverse transition, $\gamma' \rightarrow \gamma$, has never been observed.

The labels, γ , γ' , and γ'' , are those used by Erman and Gal'perin (7). These are not entirely in accord with the assignments used by Kohlmuller and Badaud (3) or those used by Chen and Smith (5). In the present paper we will assign $\gamma(\text{L})$ to a low-temperature stable phase and $\gamma(\text{H})$ to a high-temperature stable phase, to avoid further confusion. But we use the same sign γ'' , as Erman and Gal'perin, for the metastable phase.

Recently, we found out the phase transition, $\gamma(\text{H}) \rightarrow \gamma(\text{L})$, occurred when the $\gamma(\text{H})$ was heated isothermally below 640°C not at atmospheric pressure but under high pressure. In the present study, therefore, we investigated the reversible transition between the $\gamma(\text{L})$ - and $\gamma(\text{H})$ -phases by isothermal heating under high pressure, and drew

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a pressure-temperature phase diagram of Bi_2MoO_6 to establish the stability regions of $\gamma(\text{L})$ - and $\gamma(\text{H})$ - Bi_2MoO_6 . Moreover, the stability relations of $\gamma(\text{L})$ -, γ'' -, and $\gamma(\text{H})$ - Bi_2MoO_6 were discussed, and the accurate transition temperature between the $\gamma(\text{L})$ - and $\gamma(\text{H})$ -phases was estimated.

Experimental

The $\gamma(\text{L})$ - and $\gamma(\text{H})$ - Bi_2MoO_6 were used together as starting material in the equilibrium experiments. The $\gamma(\text{H})$ - Bi_2MoO_6 was prepared by heating a mixture of Bi_2O_3 and MoO_3 in a molar ratio of 1 : 1. Its X-ray diffraction pattern showed a good agreement with Chen and Smith's results (5). The $\gamma(\text{L})$ - Bi_2MoO_6 was prepared by hydrothermal synthesis. The experimental procedure for this is reported in another paper (8). The $\gamma(\text{L})$ - Bi_2MoO_6 was also prepared by isothermal heating of $\gamma(\text{H})$ at 500°C under 1000 kg/cm^2 for 48 hr. The powder X-ray diffraction pattern of this compound agreed very well with the data of the synthetic koechlinite(γ) reported by Aykan (9). About 200 mg of each modifications were charged separately in platinum capsules (4 mm o.d. and 50 mm long) and they were sealed by careful welding. The two sealed platinum capsules were set together in a pressure vessel (22 cm^3 capacity, 12 mm i.d.), as shown schematically in Fig. 1.

The pressure vessel was heated as follows: after the pressure vessel had been sealed, water was pumped into it. Then, it was set vertically within an electric furnace which had been preheated at the given temperature. The pressure was carefully controlled at a constant value until the temperature had been fixed. Temperatures were measured with a Chromel-Alumel thermocouple inserted into the pressure vessel. The experimental error was a maximum of $\pm 10^\circ\text{C}$.

After a heating run, the quenching of specimens was made by rapid soaking of

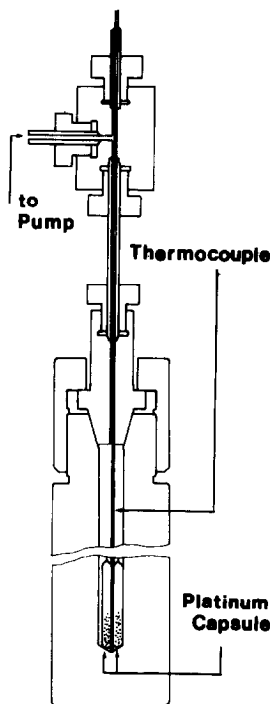


FIG. 1. The pressure vessel for isothermal heating of Bi_2MoO_6 .

the pressure vessel in water. The thermocouple inserted in the vessel indicated that the temperature fell down below 550°C within a few seconds. The quenched specimens were identified by powder X-ray diffraction analysis. A part of the experimental results are shown in Table I. Only the data obtained near the boundary between the $\gamma(\text{L})$ - and $\gamma(\text{H})$ -phases in the P - T phase diagram are shown.

Results and Discussion

Table I shows that $\gamma(\text{H})$ -modification was transformed easily into $\gamma(\text{L})$ by isothermal heating under high pressure. The heating time necessary to complete the phase transition depends on the temperature and pressure. For example, in a series of experiments at a constant pressure of 1000 kg/cm^2 and at different temperatures (500 , 400 , and 250°C), the necessary heating times were

TABLE I
EXPERIMENTAL CONDITIONS AND RESULTS

Run no.	Temp. (°C)	Pressure (kg/cm ²)	Heating time (hr)	Produced forms ^a
1	600	1000	49	γ(L)
2	635	1000	48	γ(L) γ(H)
3	617	1000	72	γ(L) > γ(H) γ(H)
4	612	1100	93	γ(L)
5	633	1100	98	γ(L) + trace γ(H) γ(H) > γ(L) γ(H)
6	606	900	103	γ(L) γ(L) + trace γ(H)
7	620	850	95	γ(H) + γ(L)
8	603	803	166	γ(H) γ(L)
9	634	800	96	γ(H) + trace γ(L) γ(H)
10	619	700	94	γ(H) γ(H)
11	585	700	70	γ(L) γ(H) > γ(L)
12	588	550	113	γ(L) γ(H) + γ(L)
13	601	505	121	γ(L) > γ(H) γ(H)
14	588	500	112	γ(L) γ(H) + trace γ(L)
15	587	450	115	γ(L) + trace γ(H) γ(H)
16	634	450	91	γ(H) γ(H)
17	605	405	143	γ(H) + γ(L) γ(H)
18	578	400	188	γ(L) γ(L) + trace γ(H)
19	571	300	192	γ(L) γ(L)
20	593	300	188	γ(H) γ(H)
21	588	200	196	γ(H) γ(H)
22	559	200	197	γ(L) γ(L) + trace γ(H)
23	563	100	191	γ(L) γ(L)
24	593	100	187	γ(H) γ(H)

^a Starting materials are corresponding in the order of γ(L) and γ(H) with produced forms in each runs.

24, 80, and more than 140 hr, respectively. In another series of experiments at constant temperature (about 400°C) and under different pressures (1500, 1000, and 800 kg/cm²), the heating times necessary for completing the phase transition were 47, 80, and 120 hr,

respectively. Therefore, it seems that the higher temperature or pressure, the faster the phase transition between γ(H) and γ(L). In the fastest case, the necessary heating time was only 2 hr (at 500°C and 1500 kg/cm²). However, in the region extremely near to the phase boundary, the transformation of Bi₂MoO₆ was very slow, even though temperature and pressure are sufficiently high (run Nos. 3, 14, and 15). Figure 2 shows the *P-T* phase diagram of Bi₂MoO₆, drawn from the data of Table I, where it is apparent that the γ(L)-form is stable in the low-temperature region and the γ(H)-form is stable in the high-temperature region at all pressures studied. As the boundary between the two regions in Fig. 2 is almost straight, we can estimate a true transition temperature between the γ(H)- and γ(L)-phases under atmospheric pressure by extrapolating the boundary. Thus, the estimated temperature was about 570°C.

The variation of transition temperature of γ-Bi₂MoO₆ with pressure can be obtained

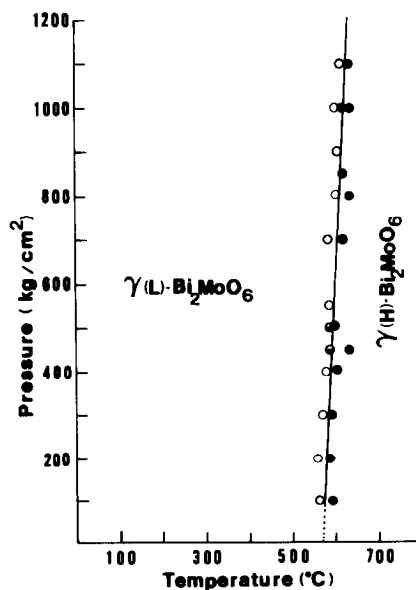


FIG. 2. The pressure-temperature phase diagram of Bi₂MoO₆.

not only from the P - T phase diagram but also by calculation. It is very interesting to compare this experimental value with the calculated one. The calculation was done by using Clapeyron's equation

$$dT/dP = T\Delta V/\Delta H. \quad (1)$$

In the case of Bi_2MoO_6 , T (the temperature of the phase transition, $\gamma(\text{L}) \rightleftharpoons \gamma(\text{H})$) equals 843°K (570°C). When densities of $\gamma(\text{L})$ - and $\gamma(\text{H})$ - Bi_2MoO_6 at the transition temperature are represented as d_l and d_h , respectively,

$$\Delta V = 1/d_h - 1/d_l \text{ (cm}^3/\text{g)}. \quad (2)$$

It has been already confirmed experimentally that the dependence of volume of Bi_2MoO_6 on temperature is so small as to be negligible (6). Therefore, the values of d_h and d_l will be replaced with the values measured at room temperature. Then, $\Delta V = 1/7.495 - 1/8.26 = 0.012365 \text{ (cm}^3/\text{g)}$, where Aykan's value (9) for d_l and Chen and Smith's value (5) for d_h were used, respectively.

ΔH is the enthalpy of the phase transition, $\gamma(\text{L}) \rightleftharpoons \gamma(\text{H})$, the value of which is already known from the DSC measurement as about 3.3 kcal/mole (6). Therefore,

$$\Delta H = 3.3 \times 10^3/609.8973 = 5.411 \text{ (cal/g)}.$$

By replacing these values with T , ΔV , and ΔH in the Eq. (1):

$$\begin{aligned} dT/dP &= (843 \times 0.01236)/ \\ &\quad 5.411 \text{ (}^\circ\text{K cm}^3/\text{cal)} \\ &= (843 \times 0.01236)/ \\ &\quad (5.411 \times 42.7) \text{ (}^\circ\text{K/kg cm}^2) \\ &= 0.045 \text{ (}^\circ\text{K/kg cm}^2). \end{aligned}$$

This result means that the temperature of the phase transition between $\gamma(\text{L})$ - and $\gamma(\text{H})$ - Bi_2MoO_6 increases by about 45°C , when pressure increases by 1000 kg/cm^2 .

As shown in Fig. 2, the observed transition temperature at the pressure, 1000 kg/

cm^2 , is about 620°C , which is about 50°C higher than the transition temperature at $P = 1 \text{ atm}$. Therefore, it is concluded that the two values of $\Delta T/\Delta P$ estimated theoretically and experimentally show good agreement.

In the present experiment, the $\gamma(\text{L})$ - and $\gamma(\text{H})$ -forms were observed but the γ'' -form was not observed. This result supports that the γ'' -form does not have a stable region in our phase diagram. As shown in Fig. 2, the $\gamma(\text{L})$ -form is a low-temperature stable phase and the $\gamma(\text{H})$ -form is a high-temperature stable phase under atmospheric pressure. The experimental data for the phase transition of the γ'' -form are given in our previous paper (6). In it we say that "the $\gamma(\text{L})$ -form transformed reversibly to the γ'' -form at 604°C , and on subsequent heating, the γ'' -form transformed irreversibly to the $\gamma(\text{H})$ -form in the range 640 to 670°C , depending on heating rates: however, an isothermal treatment at a temperature above 604°C brought the gradual transition of the γ'' -form into the $\gamma(\text{H})$ -form." On the basis of these experimental data, the relation of the phase transitions among the three forms, $\gamma(\text{L})$, γ'' , and $\gamma(\text{H})$ is shown schematically in Fig. 3. Of course, the transition, $\gamma(\text{H}) \rightleftharpoons \gamma(\text{L})$, can be observed only when heated under a higher pressure than atmospheric pressure.

The relative stabilities of the three phases, $\gamma(\text{L})$ -, γ'' -, and $\gamma(\text{H})$ - Bi_2MoO_6 depend on temperature and pressure. The relation between Gibbs's free energy and

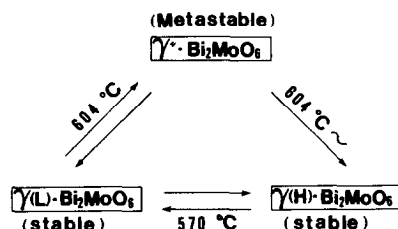


FIG. 3. The relation of the phase transitions of Bi_2MoO_6 polymorphs.

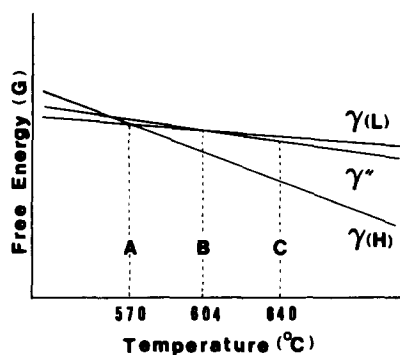


FIG. 4. A thermodynamic scheme: free energy, G , versus temperature.

temperature under atmospheric pressure is proposed schematically in Fig. 4. At the temperature below 570°C, the $\gamma(L)$ -form is the most stable form. Between 570°C (point A in Fig. 4) and 604°C (point B in Fig. 4), the relative stabilities of the three forms will increase in the order of $\gamma'' \rightarrow \gamma(L) \rightarrow \gamma(H)$. However, at the temperature over 604°C: for example, 640°C (point C in Fig. 4), it will increase in the order of $\gamma(L) \rightarrow \gamma'' \rightarrow \gamma(H)$. In the actual heating process under

the atmospheric pressure, the transition from the $\gamma(L)$ to the $\gamma(H)$ begins at considerably higher temperature than 570°C. The degree of the shift may depend on many factors such as impurities, heating rate, and so on, so that many different transition temperatures may have been reported.

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